INFLUENCE OF INDOOR MICROENVIRONMENTS AND PERSONAL ACTIVITIES ON THE INHALATION DOSE AND PERSONAL EXPOSURE TO $PM_{2.5}$, PAH, OXY-PAH, VOC AND BC AIR POLLUTANTS.

by

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ABSTRACT

Several studies have shown that in industrialized nations, subjects spend around 90 percent of their time in indoor microenvironments, (Agency, 1989, Kim et al., 2001, Harrison et al., 2009). In recent years, studies have reported the potential risk associated with indoor exposure and the effect that pollutants might cause upon subjects' health during daily activities (Bernstein et al., 2008, Ward et al., 2009). The health effect has been estimated by using ambient or indoor microenvironment concentrations. However, personal exposure measurements have been proposed as a major approach to estimate the true exposure (Buonanno et al., 2014, Li et al., 2015a, Steinle et al., 2015).

The study was part of the FIXAT project (In quest of new **FI**ngerprints of e**X**posure to **A**ir **T**oxics), whose main objectives were to characterize the personal exposure of a group of healthy, non-smoker subjects, and air quality in their home and work microenvironments to air pollutants including volatile organic compounds (VOCs) in new/old houses, $PM_{2.5}$, polycyclic aromatic hydrocarbons (PAHs), oxy-PAHs and black carbon (BC). A range of techniques were employed for physical and chemical characterization of pollutants including gravimetric analysis for $PM_{2.5}$, portable instruments for real-time $PM_{2.5}$ (RTI MicroPEM), black carbon (MicroAethalometer AE51) and online VOCs (ASU-sensor), thermal desorption coupled with a GC-MS for VOCs and solvent extraction couple with GC-MS analysis for PAH and Oxy-PAHs.

The results showed VOC concentrations to be higher for personal exposure compared with home and office microenvironment concentrations. No statistical differences were observed between old and new houses, and this is perhaps due to the fact that sampling in new houses was conducted one to three months after remodelling.

However, differences were observed in concentrations of VOC between new houses and new offices which were sampled just after the redecoration was completed. Concentrations of PAHs were found to be high for office microenvironments compared with home and personal exposure. At home, kitchen activities were the largest contributor to exposure. PAH exposure also varied by commute type with higher concentrations of PAHs for bus users followed by car users. Oxy PAHs were observed to be also high in the workplace, and this can be attributed to construction work which was carried out at the University of Birmingham during the sampling period. However personal exposure concentrations were higher than the previously reported ambient values in Birmingham. On the other hand, BC concentrations were quite high during commuting, and concentrations were found to be influenced by the commuting routes and exposure duration. BC deposited dose was found to be primarily in the alveolar region for all the analysed activities, with a bimodal size distribution (primary and secondary peaks at 0.08 µm and 0.8 µm respectively). Overall, the study highlights the importance of personal exposure concentrations as a determinant of the risk, and presents a case for further investigation on BC size fraction distribution and deposited dose.

DEDICATION

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ABBREVIATIONS

AE51	MicroAeth™

AL	Alveolar-interstitial
AM	Arithmentic mean
ANOVA	Analisis of Variance
ASU	Arizona State University
ATN	Attenuation
BB	Bronchial
bb	Bronchiolar
BC	Black Carbon
Bham	Birmingham
BROS	Bristol road observatory site
BS	Black Smoke
BTEX	Benzene, Toluene, Ethylbenzene, Xilenes
C	Concentration
CCV	Certificated concentration values
CIIT	Chemical Industry Institute of Toxicology
CPC	Condensation particle counter
DCM	Dicloromethane
DD	Deposited dose
DE	Deposition efficiency
DEFRA	Department for Environment Food & Rural Affairs
DNA	Deoxyribonucleic acid
Dp	Diameter
EC	Elemental carbon
EPA	Environment Protection Agency
EROS	Elms road observatory site
ET_1	Extrathoracic anterior nose
ET_2	Extrathoracic posterior nasal passage
ETS	Environmental Tabacco Smoke
FIXAT	In quest of new **FI**ngerprints of e**X**posure to **A**ir **T**oxics
GC-MS	Gas Chromatography/mass espectofotometry
GM	Geometric mean
GPS	Global Pisitioning System
GSD	Geometric Estándar Deviation
HMW	High molecular weight
HPLC	High pressure liquid chromatography
I/O	Indoor/outdoor
IAQ	Indoor air quality
ICRP	International commission on radiological protection
ID	Identification
ID	Inhalation dose
ID	Inhalation dose
IF	Inhalable fraction

ILD	The Instrument limit of detection
LB	Lab Blancks
LGP	Liquid Petrol Gas
LI	Lung intake
LOD	Limits of detection
LOQ	Limit of quantification
LUDEP	Lung dose Evaluation Program
MC-SIAM	Multi-compartment and size-resolved indoor aerosol model
MOUDI	Micro-Orifice Uniform-Deposit Impactor
MPPD	Multiple-Path Particle Dosimeter
MVE	Motor vehicle exhausts
NCRP	Council on Radiation Protection and Measurements
NHMRC	National Health and Medical Research Council
NIST	National Institute of Standards and Technology
NP	Nasopharyngeal
O^3	Ozono
OC	Organic Carbon
OH	Hidroxilo
ONA	Optical Noise-Reduction Averaging
OPC	Optical particle Counting
oxy-PAHS	Oxygenated-Policyclic Aromatic Hydorcarbons
PAH	Policyclic Aromatic Hydorcarbons
PE	Personal exposure
PFE	Pressurized-fluid extraction
PM	Particulate matter
ppbC	Parts Per Billon Carbon
ppbV	Parts Per Billon Volume
ppm	Part Per Millon
PSDs	Particle size distributions
PTFE	Polytetrafluoroethylene
QA-QC	Quality assurance-Quality control
RCV	Reference concentration values
SBS	Sick building Syndrome
SD	Standard deviation
SDs	Size distributions
SOP	Estándar Operation Procedures
SPMS	Scan mobility particle seizer
SMR	Standard Material Reference
SSR	Smoke Stain Reflectometer
TAD	Time Ativity Dairy
TB	Trevelling Blanks
TB	Tracheobronchial

TD	Thermal desorption
TEX	Toluene, ethybenzene and xilenes
TVOC	Total Volatic Organic Compounds
UK	United Kingdom
US-EPA	Environmental ProtectionAgency in United States of America
VE	Ventilation rate (efficiencies)
VOC	Volatile Organic Compounds
WHO	World Health Organization

CHAPTER I. INTRODUCTION

1.1 Background

The indoor environment is intuitively considered a refuge, a safe haven not only from inclement weather and temperature extremes, but also from outdoor air pollutants (Salvatore, 2003). The National Health and Medical Research Council (NHMRC) has define indoor air as

"*Air within a building occupied for at least one hour by people of varying states of health. This can include the office, classroom, transport facility, shopping centre, hospital and home*" (NHMRC, 2009).

Studies have shown that on average people spend around 90 percentage of their time in indoors microenvironments such as at home, work, school and social venues (EPA, 1989, Kim et al., 2001, Harrison et al., 2009). Since many people spend time in indoor environments, and the air quality indoors can impact the health and comfort of the occupants, researchers have had high interest in studying the indoor and personal exposure (Guo et al., 2004, WHO, 2010).

Several factors drive indoor air pollution including building design, type of ventilation system and frequency of maintenance and operation, furniture materials, moisture, humidity and age of building up (US-EPA, 1997).

Nowadays, the propagation of indoor air pollution information provided by governments, researchers, private institutions has alert the general issues population and researchers, increasing the interest of recognize the sources or activities that may negative alter the indoor quality (Bernstein et al., 2008, Liu et al., 2009a, Wheeler et

al., 2010). Moreover the attention has been focused also in public microenvironments visited by large section of the population including pubs, stores, cinemas libraries, coach, train stations, buses, trains, automobiles, schools and restaurants (Kim et al., 2001, Guo et al., 2004).

Many studies have characterized different air pollutants at the indoor environments such as PM, ozone (O_3), nitrogen dioxide (NO_2), carbon monoxide (CO), and sulphur dioxide (SO_2), VOCs, PAHs and black carbon (BC) etc. (Georgiadis et al., 2001, Wallace et al., 2003, Bernstein et al., 2008, Delgado-Saborit et al., 2009, Borgini et al., 2011, Dons et al., 2011, Horemans et al., 2012, Dons et al., 2012, Van Vliet et al., 2013, Massey et al., 2012), Which primary sources are considered to be cleaning activities, pets, pets control, renovation, incorporation of new furniture and moreover, the activities done by the occupants such cook, smoke, recreational etc. (Wallace, 1996, EPA, 1997, Yu and Crump, 1998, Bhargava et al., 2004, Wallace et al., 2003, Wallace et al., 2006, McGinty et al., 2010, Clark et al., 2010, Heroux et al., 2010, Cao et al., 2012, Liu et al., 2013b).

However, it has been state that most the indoor concentration not only depend on the indoors sources, but also it is influence by the outdoor levels (Ohura et al., 2009, Massolo et al., 2010, de Blas et al., 2012, Al-Khulaifi et al., 2014, Custódio et al., 2014, Diapouli et al., 2010, Kliucininkas et al., 2014, Lunden, 2009), which include traffic, biomass burning, industrial emissions, waste combustion, agricultural burning, etc (Han and Naeher, 2006, Baxter et al., 2008, Gao et al., 2009, Massolo et al., 2010, Awasthi et al., 2011, Pant and Harrison, 2013). Therefore studies had been done to determine the ratio of indoor- outdoor emission. The contribution of the outdoor sources into the indoors, has been reported to be between the 20 to 40 % (Abt et al.,

2000b). Concentrations of Volatile Organic Compounds (VOC), Particulate matter (PM), Black Carbon (BC) and Policyclic Aromatic Hydorcarbons (PAHs) has been reported to be higher at the indoors compared with outdoor (Edwards et al., 2001, Johnson et al., 2010, Massolo et al., 2010, Rodes et al., 2010, Serrano-Trespalacios et al., 2004, Pegas et al., 2012, Kearney et al., 2011, Masih et al., 2010). Many compounds has been well investigated in the outdoors and indoor concentrations. However, those concentrations do not reflect the personal exposure (PE), because although subjects spent more than the 60 % of the time indoors, during the day subjects develop other several activities which might increase the concentrations and the health effects. The importance to measure the personal exposure was to get a quantitative and reliable estimation of the exposure variability across microenvironments, considering that each of them will contribute to the total exposure over a time (Delgado-Saborit et al., 2009, Wheeler et al., 2010, Tiwary et al., 2011, Delgado-Saborit et al., 2011a, Chen et al., 2012, Wu et al., 2012a, Lee et al., 2013, Van Vliet et al., 2013, Buonanno et al., 2014, Choi and Spengler, 2014). The interest in characterized the personal exposure levels surge when epidemiologic studies had reported the toxicity of the pollutants base on central site concentrations, considering that the effects are underestimate because it has been reported that personal exposure concentrations are higher than the indoor and outdoor levels (Brokamp et al., 2015, Edwards et al., 2001, Serrano-Trespalacios et al., 2004, Wheeler et al., 2011).

Because of the complex activities and mixture of microenvironments visited by the subjects, a gap of information regards to the specific mechanism of how the air pollution put in risk the human health was found. Having the subject's activities and concentrations permits to establish a good relations between them, and allows to

determine the controls to decrease the exposure and risk and to developed exposure models. In addition, if the level of exercise and the particle size is include during the sampling, lung dose can be calculated, allowing to have a more complete route of exposure for the compounds (source-ambient concentration -inhalation-deposition) (Du et al., 2012).

Air pollution is considered to cause death of millions at global scale, according to the WHO, it is the major environment problem that affect the human health and place the population at risk (WHO, 2012). In 2013, the WHO declare that the outdoor air pollution is one of the leading precursors of cancer.

1.2 Sources, levels and health effects

1.2.1 $PM_{2.5}$

Physical and chemical characteristics of PM have been well investigated, because of its effects on human health (Harrison and Yin, 2000, Roberts, 2013, Rohr and Wyzga, 2012, Taner et al., 2013). Particles can be solid, liquid or both, and the health risks of PM exposure are associated with the physical attributes such as particle size as well as its chemical composition (Niu et al., 2010, Perrone et al., 2013, Taner et al., 2013, Tian Xia et al., 2004, Brokamp et al., 2015, Cho et al., 2004, Abt et al., 2000b, Choi et al., 2012, Kelly and Fussell, 2012). The health effects associated with PM are mainly attributed to particles with aerodynamic diameter less than 2.5 μm due to their ability to penetrate and deposit in the lung (Harrison and Yin, 2000, Kelly and Fussell, 2012, Wang et al., 2002, Balásházy et al., 2003). $PM_{2.5}$ exposure leads to increase levels of inflammatory markers. An also it has been found to contribute to wheezing symptoms, respiratory problems, systemic inflammation, cardiovascular problems, as well as development of the lung cancer. (Balásházy et al., 2003, Rohr and Wyzga, 2012, Strak

et al., 2010, Conti et al., 2015, Huttunen et al., 2012, Jung et al., 2012, Zhang et al., 2014, Janssen et al., 2013, Pongpiachan et al., 2015, Pope et al., 2002, Jiang et al., 2010, Anderson et al., 2012, Laumbach and Kipen, 2012). Effects on the children lung development (Gauderman et al., 2004, Pongpiachan et al., 2015, Yang et al., 2013)

A majority of the particles are generated by anthropogenic activities including vehicular emissions, which is considered the primary emission source of $PM_{2.5.}$ Indoor concentrations will primary depend on the indoor sources and also will be influence by the outdoor concentrations, therefore the location of the house will be a determinant on the obtained $PM_{2.5}$ levels. Traffic roads concentrations had been reported to be higher than background roads (Table I-1), and there are also difference in the house location, varying the concentration from urban, rural or those localized in the city centre (Cyrys et al., 2003, Kleeman et al., 2000, Pant and Harrison, 2013). Into the spatial variations China was identified to had the higher outdoor concentrations followed by Athens Greece. On the other hand, seasonal variation had also being registered by previous researchers, in general, higher concentrations were observed during the winter period, followed by spring (Table I-2). This change will also being reflected at the indoor concentrations (Perrone et al., 2013, Chithra and Shiva Nagendra, 2014, Choi et al., 2012, Kliucininkas et al., 2011, Kliucininkas et al., 2014). Moreover, research has considering the personal exposure level as important tool to assess the real contributors of exposure (Borgini et al., 2011, Brokamp et al., 2015). Although personal exposure concentrations in most of the cases had been reported higher than the indoor, outdoor and ambient (Table I-3); this is not always the case as concentration are influenced by other factors. For instance, location and weather, as previously mentioned, will alter the level of $PM_{2.5}$ and therefore the PE levels. Home

activities will impact on the PE for example in the kitchen, which variables can be cooking style, type of fire or stove, had reported to be higher concentrations compared with other house locations (Table I-4). Difference into cooking style can be observed showing the higher concentrations grilling and frying compared with toasting cooking. By far open wood and charcoal fire emitted more $PM_{2.5}$ concentrations than the used of gas or electricity. Other visited indoor or outdoor locations as well as the commute mode will influence the level of $PM_{2.5}$ exposure at the personal level Table I-5.

Table I-1 $PM_{2.5}$ concentration in µg m^{-3} by sampling location.

Reference	(Cyrys et al., 2003)			(Diapouli et al., 2010)		(Wang et al., 2015)	(Wingfors et al., 2011)			(Huang et al., 2012a)
Place	Germany	The Netherlands	Sweden	Athens		Xi'an, China	Kabul	Afghanistan	Sweden	Beijing China
characteristics	outdoor	outdoor	outdoor	outdoor	indoor	outdoor	urban	urban	City centre	urban
Background urban	13.3	17.8	10.2	20.2	16.6	167.2	86	68	7.9	
Background rural		17.3	8.4			90.2				
Traffic heavy	14.3	19.9	13.8	50.7	31.9					45.47
Traffic light										36.16
Office traffic road ambient				42.8	37.4					35.15

Table I-2 $PM_{2.5}$ concentration in µg m^{-3} by seasonal variations.

Reference	(Perrone et al., 2013)	(Anastasopoulos et al., 2012)	(Chithra and Shiva Nagendra, 2014)		(Choi et al., 2012)	(Kliucininkas et al., 2011)		(Kliucininkas et al., 2014)	
Place	Italy	Canada	Chennai India		Korea	Kaunas Lithuania		Kaunas, Lithuania,	
Characteristic	Outdoor	Outdoor	indoor	Outdoor	Outdoor	indoor	outdoor	Indoor	Outdoor
Spring	29.7				43.8	24.7	22.4		
summer	16.8	6.71	31.5	38.6	36.3			8.6	15.6
Fall	37.8				36.7				
Winter	57.3	10.7	60.9	54.8	50.9	34.5	36.7	90.9	38.7
Smog episode					73.4				

Table I-3 $PM_{2.5}$ concentration in μg m^{-3} by personal and microenvironments exposure.

Reference	(Meng et al., 2012)		(Michikawa et al., 2014)		(Georgiadis et al., 2001)		(Borgini et al., 2011)	(Van Vliet et al., 2013)	(Abt et al., 2000a)	(Franck et al., 2011)	(Du et al., 2010)	(Jahn et al., 2013)
Place	**Michigan US**		**Tokyo Japan**		**Athens Greece**		**Italy**	**Ghana**	**Boston US**	**Leipzig Germany**	**Beijing China**	**China**
characteristics	**summer**	**winter**	**Ichikawua**	**Toride**	**winter**	**summer**						
Home			17.1	24.4					13.9	29.8		
Personal	20.9	19.6			46.4	35.8	75.94	8.8			102.5	71.9
Ambient	17.6	15.3	17.8	33.3			65.28				118.5	
Outdoors			18.5	31.2					64			77.7

Table I-4 $PM_{2.5}$ concentration in µg m^{-3} by home microenvironments.

Reference	**(Yassin et al., 2012)**	**(Titcombe and Simcik, 2011)**			**(Lim et al., 2012)**						**(He et al., 2004)**				
Place	**Kuwait**	**Tanzania**			**Seoul, Korea**						**Brisbane, Australia**				
characteristics		**LPG**	**Charcoal and kerosene**	**charcoal**	**Open wood fire**	**Charcol in table**	**Gas in table**	**kitchen**	**Electric stove cooking**	**frying**	**grilling**	**Microweve**	**oven**	**stove**	**Toasting**
Kitchen	63.07	14	88	588	1574	388	49	22	18	37	745	3427	16	24	57	35
Living room	44.6															
bedroom	25.90															

Table I-5 $PM_{2.5}$ concentration in μg m^{-3} by microenvironments.

Reference	(Lim et al., 2012)	(Wallace et al., 2006)	(Steinle et al., 2015)	(Apte et al., 2011)	(Du et al., 2010)	(de Nazelle et al., 2012)	(Huang et al., 2012a)	(Du et al., 2010)
Place	**Seoul Korea**	**N. Carolina US**	**Scotland UK**	**India**	**Beijing China**	**Barcelona Spain**	**Beijing China**	**Beijing China**
characteristics								
Office	21.2		3.0		115			
restaurant	188.5							
pub	69.4							
school	15.5							
Transportation	18.6	33.6	7.0	200				
walk						21	49.10	91.8
Bike						29	42.40	
Bus						25	31.64	129.2
car						35		

1.2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are formed by incomplete combustion of the organic substances and can be found in gas or particulate phase. Typically, high molecular weight PAHs, i.e. those with five or six rings are found in the particle phase while the low molecular weight PAHs such as those with three and two rings exist predominantly in the gas phase (Rajput and Lakhani, 2009, Liu et al., 2010).

The major source of many of these PAHs, such as benzo(c)phenanthrene, Benzo(b)fluoranthene (B[b]F), Benzo(a)pyrene (B[a]P), and Benzo(b)napth (2,1-d) thiophene which have 4–6-ring are vehicle exhaust (Harrison et al., 1996, Kuo et al., 2003, Wickramasinghe et al., 2012). Other outdoor sources of PAHs are industrial oil plants which emit principally pyrene (Pyr) and chrysene (Chry) as well as the power generation plants, waste incinerators and open burning Fluoranthene (Fluo) and pyrene are typically emitted by both petrol and diesel vehicles, and chysene (Lavanchy et al.), benzo (b)fluoranthene (B[b]F), benzo (k)fluoranthene (B[k]F) are characteristic of emissions from diesel vehicles (Rajput and Lakhani, 2009, Choi et al., 2010, Kliucininkas et al., 2011). Semi volatile 3–4-ring PAHs—Phenantrene (Ph), Anthracene (An), Fluorene (Fl), and Chrysene (Chry), are also associated with cooking and heating (Harrison et al., 1996, Kuo et al., 2003). Some of the indoor sources are cooking, smoking, natural gas burning, liquid petroleum gas, kerosene, wood, dung, coal and, candles, incense and filtrations from the outdoor (Choi et al., 2010, Masih et al., 2010).

Ambient PAH concentrations can vary based on the solar radiation, ambient temperature and humidity, resulting in a photochemical atmospheric reaction causing a photolytic degradation, or different gas-particle partitioning (Kamens et al., 1988, Liu et al., 2013a). Research has found higher concentration during the heating time

(summer) than in the cold time (winter) (Table I-6) (Narváez et al., 2008, Guzmán-Torres et al., 2009, Jung et al., 2010, Masiol et al., 2013). However, higher concentrations of PAHs can be observed during the cold season by accumulation on the lower atmospheric layers (Masiol et al., 2013). Day- night studies had reporting higher concentrations of particulate PAHs during the night, however diurnal high concentrations were reported for gas-phase (Table I-7) (Liu et al., 2013a, Souza et al., 2014). In the absence of random activities, outdoor infiltration to the indoors will depend on the type of building, construction materials, conditions of the building (Aquilina et al., 2010, Choi et al., 2010). Moreover, the PAHs levels also depend on the activities developed in the building such cook, clean or even relax (e.g. candle burning). However the indoor high concentrations are reported to be emitted from the kitchen followed by living room. The cooking style than provides most PAHs concentrations is frying and the wood fire also raise the level of PAHs compared with gas (Table I-8). On general, indoor microenvironment concentrations were found to be higher for Agar, India (Masih et al., 2010) compared with Birmingham (Harrison et al., 2009) or Japan (Ohura et al., 2005). Within the microenvironments the kitchen registered the higher concentrations compared with living room and bedroom (Table I-9). And PAHs have been also found to had higher concentrations in pubs and restaurants (Liu et al., 2009b, Masih et al., 2010, Delgado-Saborit et al., 2011b, Křůmal et al., 2013, Krugly et al., 2014). Several studies had recorded the effect of being exposed to ETS over the PAHs concentrations at the indoor and personal exposure level. Findings indicate that the ETS will increase the concentrations of PAHs (Table I-10).

People are exposed to PAHs primarily from the respiratory system, considering the primary route of exposure the nose, however other routes cannot be discharged (Liu et al., 2010, Zhang et al., 2012, Kim et al., 2013). Breathing ambient or indoor air, smoking or being in contact with smokers or inhaling smoke from open fireplaces can lead to a deposition of PAHs in the respiratory tract, causing respiratory diseases in healthy people or increasing the risk in people with previous respiratory problems (Bernstein et al., 2008, Zhao et al., 2011, Zhou and Zhao, 2012). PAHs has been associated with asthma (Suresh et al., 2009), pulmonary illnesses, and pulmonary tuberculosis (Bhargava et al., 2004), reproductive, developmental, neurological, respiratory, cardiovascular outcomes (Johnson et al., 2010) and peripheral arterial disease (Xu et al., 2013). It has been reported that PAHs such B[a]A, Chry, B[b]F, B[k] and B[a]P might have carcinogenic and mutagenic properties (Liu et al., 2010, Luch and Baird, 2010, Masiol et al., 2012, Carreras et al., 2013, Khairy and Lohmann, 2013, Xia et al., 2013, Zhu et al., 2014), PAHs can also generate DNA or oxidative damage (Umbuzeiro et al., 2008, Tang et al., 2014). Moreover, PAHs that has been absorbed into the body can be metabolized to their mono hydroxylated PAHs (Aquilina et al., 2010).

Table I-6 Outdoor PAHs concentrations (ng m^{-3}) in trafficked roadside and seasonal variations.

Location	Agra India	Tuscany Italy	Manhattan US	Kaunas Lithuania	Birmingham UK	Marseilles France	Tuscany Italy	Manhattan US	Munich Germany
Site type	Road side	Urban traffic	Traffic	Urban traffic	Urban traffic	Urban traffic	Urban traffic	Traffic	Urban traffic
	Cold season					Warm season			
Compound	(Masih et al., 2010)	(Martellini et al., 2012)	(Jung et al., 2010)	(Kliucininkas et al., 2011)	(Saborit et al., 2009)	(Albinet et al., 2007)	(Martellini et al., 2012)	(Jung et al., 2010)	(Schnelle-Kreis et al., 2001)
Naphthalene									
Acenaphthalene									
Acenaphthene									
Fluorene	71.2	0.5				1.09	0.03		
Phenanthrene	110	0.5	25.1	1.3		8.5	0.38	8.4	
Anthracene	17.9	0.6		0.2		0.76	0.09		
Fluoranthene	33.0	0.6		7.6		3.5	0.69		0.8
Pyrene	29.2	0.9	1.1	9.5	0.2	5.8	0.88	0.8	0.8
Benzo(a)thnthracene	31.3	1.2	0.07	7.0		0.07	0.83	0.1	
Chrysene	33.3	1.2	0.1	9.2	0.3	0.2	0.84	0.3	0.8
Benzo(b)fluoranthene	35.7	1.3	0.2	5.8	0.3	0.6	0.40	0.6	1.62
Benzo(k)fluoranthene	18.4	1.1	0.06	5.6		0.08	0.33	0.2	
Benzo(e)pyrene	19.8	0.6			0.2	0.4	1.3		
Benzo(a)pyrene	28	1.0	0.08	6.2	0.2	0.1	0.21	0.2	0.7
Indeno(1,2,3-cd)pyrene		0.9		9.6	0.04	0.2	0.14		
Dibenz(a,h)anthracene		0.8		2.3		0.02	0.23		
Benzo(ghi)perylene	21.6	0.5		6.1		0.2	0.01		0.9
Coronene									

Table I-7 PAHs concentrations (ng m^{-3}) by seasonal variations.

Location	São Paulo, Brazil		Beijing, China		Shandong, China		New York, US			
	Rural				background		indoor		winter	
	day	night	winter	summer	winter	summer	summer	winter	indoor	outdoor
Reference	(Souza et al., 2014)		(Wu et al., 2014)		(Zhu et al., 2014)		(Jung et al., 2010)		(Kliucininkas et al., 2011)	
Compound										
Naphtalene										
Acenaphthalene	0.3	0.1			0.2	0.08				
Acenaphthene					0.4	0.2				
Fluorene	0.04	0.06	0.05	0.02	2.03	2.00				
Phenanthrene	0.2	0.02	0.8	0.05	2.8	0.7	32.7	56.6	1.3	1.2
Anthracene		0.3	0.8	0.05	0.5	0.1			0.2	0.2
Fluoranthene	0.4	2.1	9.1	0.6	6.4	2.02			7.6	3.5
Pyrene	0.3	0.9	3.1	0.2	4.04	1.2	1.09	1.6	9.5	3.9
Benzo(a)thnthracene	0.1	1.6	3.4	0.5	1.9	0.1	0.1	0.07	7.0	2.8
Chrysene	0.2	0.6	8.2	2.8	1.7	0.07	0.1	0.09	9.2	4.5
Benzo(b)fluoranthene	0.3	2.9	5.5	2.0	0.04	0.05	0.3	0.2	5.8	3.0
Benzo(k)fluoranthene					7.2	0.2	0.1	0.06	5.6	3.1
Benzo(e)pyrene										
Benzo(a)pyrene	0.1	0.3	4.8	1.7	2.2	0.03	0.2	0.2	6.2	3.2
Indeno(1,2,3-cd)pyrene			35.3	1.9	2.4	0.1			9.6	2.6
Dibenz(a,h)anthracene					0.09	0.1	0.04	0.03	2.3	0.7
Benzo(ghi)perylene			10	1.7	2.06	0.1	0.7	0.9	6.1	2.6
Coronene										

Table I-8 PAHs concentrations (ng m^{-3}) in kitchen.

Location	Taipei, Taiwan			Tanzania, EastAfrica			Lucknow India	
Site type	cooking type (LPG)			fuel type			cooking	
characteristics	Boiling	heating	frying	LPG	kerosene/charcoal	Wood fire	wood	LPG
	(Zhao et al., 2011)*			(Titcombe and Simcik, 2011)			(Bhargava et al., 2004)	
Naphthalene	3.6	1.9	10.1					
Acenaphthylene	2.7	1	8.4					
Acenaphthene	6.1	4.5	7.6					
Fluorene	7.8	5.3	6.3					
Phenanthrene	14.2	11.9	22.6	1.12	1.0	73.3		
Anthracene	4.3	3.0	6.7		0.06	22.04		
Fluoranthrene	36.9	10.9	59.9		3.9	210.5		
Pyrene	47.2	29.7	63.5		5.4	225.8		
Benzo(a)anthracene	103.9	79.6	185		5.8	193.3	560	260
Chrysene	53.3	39.7	69.3		4.9	228.6	3570	600
Benzo(b)fluoranthene					8.3		830	210
Benzo(k)fluoranthene	57.7	37.6	90.1				950	210
Benzo(e)pyrene								
Benzo(a)pyrene	38.7	26.5	66.3		4.2	273.5	700	290
Indeno(1,2,3-cd)pyrene	155.7	107.8	177.6		3.4	387.7	1000	300
Dibenz(a,h)anthracene	23.9	17.3	31.4		2.0	402.4	1560	320
Benzo(ghi)perylene	11.5	8.8	15.7		5.02	491.8		
Coronene								

Table I-9 PAHs concentrations (ng m^{-3}) by microenvironment.

Location	Birmingham, UK							Shizuoka, Japan					Agra, India		Island of Fyn, D	
Characteristics	street	transport	stations	Pubs and restaurant	Other indoor	home	work place	Living room	kitchen	bedroom	workplace	outdoor	kitchen	living room	home	nursery
Reference	(Harrison et al., 2009)							(Ohura et al., 2005)					(Masih et al., 2010)		(Langer et al., 2010)	
Naphthalene	0.15	0.56	0.23	0.32	0.53											
Acenaphthylene													148	152		
Acenaphthene	0.44	2.63	0.43	1.22	1.15	0.1	0.1						26.2			
Fluorene	0.38	0.33	1.00	0.53	0.88	0.5	0.4	0.2	0.17	0.14	0.21	0.2	59.9	32.7		
Phenanthrene	1.54	0.19	0.21	0.41	-	0.6	1.0						67.0	31.3		
Anthracene	0.50	0.83	0.49	0.50	1.14	0.2	0.2							43.8		
Fluoranthrene	0.10	0.25	0.09	0.14	0.29	0.05	0.08						16			
Pyrene	1.76	2.41	1.50	1.62	2.16	0.5	0.8	0.22	0.22	0.21	0.22	0.24	13.2		120	105
Benzo(a)anthracene	0.77	1.66	0.95	1.04	0.85	0.4	0.4	0.08	0.09	0.09	0.1	0.13	21.8	54	18.0	13.0
Chrysene	0.09	0.37	0.12	0.32	0.04	0.06	0.1	0.20	0.2	0.2	0.21	0.26	17.4	48.1		
Benzo(b)fluoranthene	0.26	0.88	0.31	0.23	0.34	0.2	0.3	0.32	0.30	0.28	0.35	0.37	23.9	71.4		
Benzo(k)fluoranthene	0.17	0.51	0.26	0.66	0.12	0.2	0.5	0.13	0.12	0.12	0.14	0.16				
Benzo(e)pyrene								0.24	0.22	0.21	0.26	0.27	20.0	30.5		
Benzo(a)pyrene	0.16	0.36	0.16	0.57	0.11	0.2	0.3	0.3	0.24	0.23	0.25	0.28	13.1	37.8	10.0	13.0
Indeno(1,2,3-cd)pyrene	0.13	0.28	0.12	0.27	0.05	0.09	0.2									
Dibenz(a,h)anthracene	0.15	0.23	0.18	0.26	0.08	0.1	0.2	0.03	0.03	0.03	0.03	0.03				
Benzo(ghi)perylene	0.02	0.02	0.01	0.11	-	0.02	0.02	0.32	0.29	0.29	0.33	0.33	13.1			
Coronene	0.20	0.43	0.30	0.53	2.45	0.2	0.3	0.13	0.13	0.13	0.16	0.15				

Table I-10 PAHs concentrations (ng m^{-3}) personal exposure.

Location	Shizuoka, Japan	Birmingham UK	Birmingham UK		Madrid Spain
characteristics	No ETS	No ETS	ETS	No ETS	Semi-urban
Reference	(Ohura et al., 2005)	(Harrison et al., 2009)	(Aquilina et al., 2010)		(Barrado et al., 2013)
Naphthalene					0.01
Acenaphthylene		0.5	0.18	0.23	
Acenaphthene		0.6	0.25	0.20	0.006
Fluorene	0.10	0.5	0.22	0.25	0.02
Phenanthrene		0.5	0.21	0.18	0.15
Anthracene		0.1	0.05	0.04	0.02
Fluoranthrene		0.9	0.37	0.35	0.25
Pyrene	0.22	0.6	0.25	0.17	0.25
Benzo(a)anthracene	0.61	0.5	0.05	0.09	0.09
Chrysene	0.16	0.8	0.18	0.38	0.2
Benzo(b)fluoranthene	0.29	0.7	0.14	0.22	0.14
Benzo(k)fluoranthene	0.13	0.7	0.13	0.21	0.06
Benzo(e)pyrene	0.24				
Benzo(a)pyrene	0.24	0.6	0.08	0.13	0.07
Indeno(1,2,3-cd)pyrene		0.5	0.09	0.11	
Dibenz(a,h)anthracene	0.03	0.06	0.13	0.17	
Benzo(ghi)perylene	0.34	0.6	0.02	0.04	
Coronene	0.14	0.3	0.09	0.12	

1.2.3 Oxy PAHs

The derivative PAHs are normally less volatile than the parent PAHs (Kamens et al., 1989, Kameda, 2011, Cochran et al., 2012, Delgado-Saborit et al., 2013) high molecular weights and low vapour pressure characterized these compounds (Sienra, 2006, Walgraeve et al., 2010). As a result of that, they are easily deposited on the particles. Albinet et al., (2006) reported that the 9,10- Antraquinone and the 9-fluorenone were common oxy-PAHs associated with the particle phase. The oxy-PAHs have in the aromatic structure one or more oxygen attached to the aromatic ring (Shen et al., 2011).

The derivate PAHs compounds are normally formed from the incomplete combustion of fossil fuels generated by the industry, diesel, heat waste incineration and natural source such as forest fires, solid fuel as crop, residues and coal combustion (Pandey et al., 2011, Ringuet et al., 2012, Oda et al., 2001, Kameda, 2011, Shen et al., 2011). Thus, oxy-PAHs are also formed by the reaction of the parent PAHs and the O_3, OH, NO radicals in a photo oxidation process also known as a secondary formation process, this can lead with high concentration of oxy-PAHs during the day compared with night (Albinet et al., 2007, Walgraeve et al., 2010, Ringuet et al., 2012). Oxy-PAHs can also experience photochemical decomposition influenced by the UV irradiation. The photolysis rate of oxy-PAHs has been measure to determine the atmospheric lifetime of the compound. Results indicate high stability of oxy-PAHs to the photodecomposition, which at the end will be reflected in a prolonged human exposure to oxy- PAHs and therefore high risk. Although the oxy-PAHs decay with the light their photo-decomposition is lower than the nitro-PAHs rate (Tsapakis and Stephanou, 2007, Kameda, 2011, Kamens et al., 1989). Oxy-PAHs have been reported to form

DNA adducts and can cause oxidative stress, alterations of lung epithelial cells and in some cases can cause mitochondrial dysfunction (Tian Xia et al., 2004, Umbuzeiro et al., 2008).

Similar to PAHs, higher concentrations of oxy- PAHs have been reported in China and Japan and because the primary source is the traffic emissions the studies had focused to determine the levels at different locations and traffic intensity (Table I-11). Winter concentration were found to be higher at Santiago, Chile compared with Birmingham UK (Table I-12).

Table I-11 Oxy-PAHs concentrations (ng m^{-3}) by locations.

Location	Massachusetts US	Palaiseau France	Marseilles France		Birmingham UK	China	Birmingham (UK)		Afghanistan
Site type	Urban	Sub urban	Urban	Rural		urban	traffic	Back ground	Back ground
Reference	(Allen et al., 1997)	Ringuet et al., 2012)	(Albinet et al., 2007)		(Delgado-Saborit et al., 2013)	(Bandowe et al., 2014)	(Alam et al., 2013a)		(Wingfors et al., 2011)
1,4-Naphthoquinone					0.065	4.4	2.08	0.82	0.2
2,6-di-tert-butyl-1,4-Benzoquinone					1.9				
2-methyl-1,4-Naphthoquinone					0.08		1.50	0.67	
Acenaphthenequinone					0.07				
9,10 anthraquinone	0.4	0.7	1.4	0.2	1.8	4.84	0.93	0.50	2.4
2-methyl-anthraquinone					0.5	0.28	2.82	0.49	
2,3-dimethyl-anthraquinone					0.1		0.33	0.31	
Benz[a]anthracene7,12-dione			0.1	0.1	0.5	4.36	0.48	0.38	3.1
5,12-naphthacene-quinone	0.3	0.05			0.3	2.54	0.55	0.40	

Table I-12 Oxy-PAHs concentration (ng m^{-3}) at urban and considering the seasonal variation.

Location	Japan					Weybourne UK		Santiago Chile		Araraquara Brazil	
Site type	Urban tunnel					Rural		Urban		Rural	
Characteristics	Site 1	Site 2	Site 3	Site 4	Site 5	winter	summer	winter	spring	diurnal	nocturnal
Reference	(Oda et al., 2001)					(Alam et al., 2013a)		(Sienra, 2006)		(Souza et al., 2014)	
1,4-Naphthoquinone	0.68	0.81	0.95	0.80	0.37	0.016	0.033	0.3			
2,6-di-tert-butyl-1,4-Benzoquinone											
2-methyl-1,4-Naphthoquinone						0.015	0.011				
Acenaphthenequinone	1.5	1.9	0.80	0.68	0.88						
9,10 anthraquinone	29	41	53	56	35	0.055	0.044	1.6	0.6	1.0	0.7
2-methyl-anthraquinone	4.8	5.7	6.4	7.4	5.0	0.051	0.042				
2,3-dimethyl-anthraquinone						0.040	0.029				
Benz[a]anthracene 7,12-dione						0.021	0.014	1.8	0.5		
5,12-naphthacene-quinone	0.48	1.0	1.6	1.3	0.62	0.022	0.015	1.4	0.3		

1.2.4 Volatile Organic Compounds (VOC)

The major source of VOCs is reported to be vehicular exhaust and industrial emissions, which might affect not only to surroundings ambient but also to the car cabin people. Moreover exhaust vehicular emissions has been found at indoor microenvironments which do not have attached garages, suggesting possible penetration from outdoors (Kim et al., 2001, Bruno et al., 2008, Guo et al., 2009, Brodzik et al., 2014). There is a highly correlation between compounds such ethylbenzene, o-xylene, toluene, m, p-xylene, trimethylbenzene, hexane and benzene with vehicular emission (Edwards et al., 2001, Kim et al., 2001). Therefore the house location has been considered in several studies, with the common aim to determine the concentration difference between; rural, urban and city centre, traffic or background road and estimate the factor that might contributes more to the levels of VOCs exposure (Saborit et al., 2009, Jung et al., 2011, Byun et al., 2010). By far, China has reported the higher values at the outdoors traffic road, followed by Korea which samples were obtained from an industrial area (Table I-13).

Seasonal variation has also been reported, however this variations depend on the source and emission rate of the compound. Table I-14 show seasonal outdoor concentration achieved at diverse places. Hong Kong, China displayed the higher VOC concentrations followed by Tianjin, China and New Jersey, US. Divergent results have been reported, indicating higher concentration in winter, while other had reported the opposite, displaying higher levels in summer. However what can be observed in the outdoor concentrations is a season variation across the VOC compounds, which denote that the meteorological variations affect distinctively at each VOC compound

(Stocco et al., 2008, Sofuoglu et al., 2010, Edwards et al., 2001, Ho et al., 2004) (Table I-15).

The major indoor VOCs sources are reported to be cleaning products, perfumes, particleboard and household products such varnishes, solvents, adhesives (Edwards et al., 2001, Guo et al., 2009, de Gennaro et al., 2014, Rahman and Kim, 2014, Kim et al., 2001). Moreover, building materials, furniture, appliances may release benzaldehyde and octanal which also is related with mould (Wolkoff, 1995, Bernstein et al., 2008, Byun et al., 2010). Significantly emission of VOC is related with the indoor activities developed by the inhabitants. For instance, higher concentrations had been found with subjects cooking (Guo et al., 2009, Byun et al., 2010). In addition to this, the cooking style might alter the VOC levels at the indoors (D'Souza et al., 2009, Wang et al., 2009). Concentration of home microenvironments are illustrated in Table I-16, on general, higher concentration were obtained for Korea and Birmingham, however, as revelled by the numbers Birmingham home concentration in 2001 were higher than the posterior measurements that were performed in 2009, 2011 and 2012.

Considering that subject not only spent time at their home, researchers have also been interested in measuring other indoor-outdoor microenvironments to determine how VOC contribute to the personal exposure. Although several information is available, this is not enough to characterize or compare the microenvironments concentrations due to the diversity of microenvironments. The most common indoor sample site are restaurant, pubs, schools, and office, (Guo et al., 2004, Kim et al., 2001, Zhou et al., 2011, Wang et al., 2009). Currently the microenvironments that had registered higher concentration are restaurant and pubs (Table I-17). Additionally, subjects also spent time for commute, the level of exposure depend on the transport media used, for

instance, according the previous results, travelling by car will increase the exposure VOC levels compare with bus or train (Kim et al., 2001, Zhou et al., 2011). Other factor that has been study is the difference between smokers and non-smokers, as significant difference has been reported in the level of VOC. Consequently, not smoker subjects had been tested on the ETS exposure at home or work microenvironments, resulting in higher level for those having ETS exposure, considering this as other contributor of the personal exposure (Table I-18).

Volatile Organic Compound (VOCs) on air enters the body via inhalation (Yamamoto et al., 2010, Kliucininkas et al., 2014). Exposure to VOC can derivate a wide range of acute and chronic health effects such fatigue, concentration difficulties (DeJongh et al., 1998, Bernstein et al., 2008), headaches, dizziness, nausea, lethargy, which normally are considered as neurological symptoms (Guo et al., 2004, Huang et al., 2011) irritation of the nervous system and asthma (Delgado-Saborit et al., 2009, Ward et al., 2009, Zhou et al., 2011). The acute exposure of some VOCs may not be harmful to human health, when the exposure is short. However, the long-term exposure may cause mutagenic and carcinogenic effects (Guo et al., 2004, Massolo et al., 2010).

Table I-13 Outdoor VOC concentration reported in the literature (μg m^{-3}).

Location	La Plata Argentina	Canosa di Puglia Italy	Hong Kong China	Hong Kong China	Bham UK	Helsinki Finland	Korea	La Plata Argentina			
Site type	General	Site 1	Traffic road	Traffic road	Traffic Road	General	General	industry	Urban	Semi-rural	residential
Reference	(Colman Lerner et al., 2012)	(Bruno et al., 2008)	(Chan et al., 2002)	(Ho et al., 2002)	(Kim et al., 2001)	(Edwards et al., 2001)	(Shin and Jo, 2012)	(Massolo et al., 2010)			
Benzene	3.15	6.0	26.7	4.85	49.6		1.9	13.42	3.06	1.71	1.52
Toluene	8.82	17.1	77.2	28.81	108.1	3.35	31	18.90	6.53	3.04	2.76
Ethylbenzene	1.15	4.4	3.1	3.11	12.4		3.5	1.80	1.01	0.41	0.66
p-xylene	6.94	12.7	12.1	3.98	11.6	2.16	5.2	10.91	6.31	2.22	2.50
m-xylene		6.1			32.3						
pyridine											
o-xylene	1.27	4.2	4.6	2.85	13.2	1.40	1.4	2.30	1.13	0.45	0.73
Cumene											
Dipentene	1.25		0.2								
n-propylbenzene											
Styrene	0.17	1.2	1.8		1.7		1.0	0.13	0.12	0.07	0.01
p-isopropyltoluene		2.5									
1,3,5-trimethylbenzene		3.6			2.8	1.73	1.3				
1,2,4-trimethylbenzene		0.9					1.4				
1,2,3-trimethylbenzene							0.8				
Benzaldehyde						1.76					
Octaldehyde						2.53					
2-ethyl-1-hexanol						1.42					
Naphthalene	0.42						0.9	0.13	0.12	0.05	0.06

Table I-14 Outdoor VOC concentration reported in the literature (μg m^{-3}).

location	New Jersey US		Ontario Canada		Tijuana México	Kaunas Lithuania		Tianjin China	Michigan US	Hong Kong China	
Site type	Summer	Winter	Summer	winter	spring	winter	spring	Summer	Fall	Winter	Summer
Reference	(Wu et al., 2012b)		(Stocco et al., 2008)		(Zheng et al., 2013)	(Kliucininkas et al., 2011)		(Zhou et al., 2011)	(Johnson et al., 2010)	(Ho et al., 2004)	
Benzene	1.55	1.15	0.97	0.7	0.5	0.9	1.0	3.89	1.7	5.07	2.97
Toluene	2.48	2.77	2.51	5.3	0.9	2.7	2.0	1.89	4.4	26.44	26.22
Ethylbenzene	0.40	0.47		0.1	0.2	0.2	0.3	2.23	0.8	2.61	3.18
p-xylene	1.24	1.45	0.85					2.45	2.8	2.78	3.99
m-xylene											
Pyridine											
o-xylene	0.44	0.50						0.30	1.0	2.03	3.06
Cumene											
Dipentene			0.03								
n-propylbenzene											
Styrene	0.12	0.13						0.23	0.3		
p-isopropyltoluene											
1,3,5-trimethylbenzene								0.31		0.79	1.39
1,2,4-trimethylbenzene										2.15	2.59
1,2,3-trimethylbenzene											
Benzaldehyde											
Octaldehyde											
2-ethyl-1-hexanol											
Naphthalene				0.2	0.1	0.2	0.2				

Table I-15 Indoors VOC concentration reported in the literature (μg m^{-3}).

Location	Perth Australia		Canada	Ontario Canada		Kaunas Lithuania		Tianjin China	La Plata Argentina			
Site type	Summer	Winter	General	Winter	Summer	Winter	Spring	Summer	industry	Urban	Semi-rural	residential
Reference	(Maisey et al., 2013)		(Zhu et al., 2013b)	(Stocco et al., 2008)		(Kliucininkas et al., 2011)		(Zhou et al., 2011)	(Massolo et al., 2010)			
Benzene			1.9	1.7	2	0.7	0.5	6.1	18.0	3.20	3.14	3.10
Toluene	2.6	10.1	17.8	12	30.1		0.9	7.5	20.81	11.70	9.44	9.51
Ethylbenzene	0.2	1.4	4.2			6.1	0.2	1.3	2.13	1.27	0.97	1.66
p-xylene	0.42	2.08	14.4	4.4	11.2	7.5		1.6	10.16	6.33	3.82	4.44
m-xylene						1.3						
Pyridine						1.6						
o-xylene	0.32	2.5	4.3					0.5	3.04	1.42	0.97	1.43
Cumene	0.1	0.1										
Dipentene	1.8	2.4		9.9	19.8	0.5						
n-propylbenzene												
Styrene	0.07	6.3	1.1					0.3	0.25	0.20	0.18	0.16
p-isopropyltoluene												
1,3,5-trimethylbenzene						0.3		0.2				
1,2,4-trimethylbenzene			1.4									
1,2,3-trimethylbenzene			4.3			0.2						
Benzaldehyde			4									
Octaldehyde												
2-ethyl-1-hexanol	0.37	0.17										
Naphthalene			6.6			0.2	0.1		0.58	0.23	0.26	0.31

Table I-16 Indoors VOC concentration reported in the literature (µg m^{-3}).

Location	Birmingham UK	La Plata Argentina	Birmingham UK	Birmingham UK	Michigan US	Korea	Hong Kong China
Site type	Home	Home	Home	Home	Home	New house	home
Reference	(Delgado-Saborit et al., 2011a)	(Colman Lerner et al., 2012)	(Harrison et al., 2009)	Kim et al., 2001)	(Johnson et al., 2010)	(Shin and Jo, 2012)	(Guo et al., 2009)
Benzene	12	2.4	1.5	14	3.0	3.9	
Toluene	17.5	7.5	11	38.4	18.0	184	15.3
Ethylbenzene	1.7	1.4	1.2	2.3	2.3	8.2	4.1
p-xylene	1.7	6	1.03	1.9	7.9	14	3.0
m-xylene	4.1		2.6	5.3			
Pyridine	0.2		0.1	0.4		2.8	
o-xylene	2.02	1.7	1.3	1.9	2.7		
Cumene							
Dipentene		13.4					
n-propylbenzene							
Styrene	0.9	0.1	0.6	0.8	1.6	2.7	11
p-isopropyltoluene	1.03		0.8				
1,3,5-trimethylbenzene	0.6		0.4	0.5		6.5	
1,2,4-trimethylbenzene	2.3		1.3			3.1	5.4
1,2,3-trimethylbenzene						3.3	
Benzaldehyde							
Octaldehyde							
2-ethyl-1-hexanol							
Naphthalene	0.8	3.7	0.5	0.8		0.8	

Table I-17 Microenvironments VOC concentration reported in the literature (µg m^{-3}).

Location	Birmingham UK					New Jersey US	Finland	Barcelona Spain	Tianjin China		Bham UK		Bielsko-Biała, Poland
Site type	office	rest	Car	Train	buses	Airport	Waste treatment plant	Waste treatment plant	Office	Vehicle	Workplace	Pubs and restaurant	In vehicle
Reference	(Kim et al., 2001)					(Jung et al., 2011)	(Lehtinen et al., 2013)	(Gallego et al.)	(Zhou et al., 2011)		(Harrison et al., 2009)		(Brodzik et al., 2014)
Benzene	5.9	22.7	203.7	64.9	20.2	0.84		40	1.38	2.34	1.05	1.94	8.4
Toluene	38.4	57.0	494.0	5.6	69.3	3.21		16.5	1.46	2.73	3.54	6.14	28.7
Ethylbenzene	2.4	6.2	51.9	4.8	8.0	0.30	0.04	417	0.30	0.88	0.85	1.03	7.5
p-xylene	1.7	5.6	52.5	13.2	7.6	0.99	0.09	1257	0.47	1.42	0.78	0.78	7.4
m-xylene	6.0	16.3	127.2		20.3						1.97	2.27	19.8
Pyridine		0.6	1.7	5.0							0.10	0.89	
o-xylene	1.8	6.0	54.2		8.6	0.34		331	0.07		0.92	1.01	
Cumene													
Dipentene							1.20						
n-propylbenzene				1.4				84					3.1
Styrene	0.6	1.4	4.3		0.7			121	0.08	0.20	0.48	0.56	
p-isopropyltoluene				1.0							0.33	0.78	
1,3,5-trimethylbenzene	0.3	1.3	9.4		2.3			125	0.05	0.42	0.22	0.23	2.1
1,2,4-trimethylbenzene								656			0.78	0.96	6.0
1,2,3-trimethylbenzene								222					3.7
Benzaldehyde								280					
Octaldehyde													
2-ethyl-1-hexanol				1.0									13.6
Naphthalene	1.7	0.9	5.0	1.0	0.9			42			0.33	0.32	6.6

Bhma-Birmingham

Table I-18 Personal exposure VOC concentration reported in the literature (µg m^{-3}).

Location	Montana US		Seoul Republic of Korea	Bham UK	Republic of Korea	United Kingdom				Tianjin China	Bham UK	Mexico
Sampling type	Smoker or ETS	Non smoker	In children	No smokers		Urban	Rural	ETS	Non-ETS			
Reference	(Wang et al., 2009)		(Byun et al., 2010)	(Delgado-Saborit et al., 2011a)	(Jo and Kim, 2010)	(Saborit et al., 2009)				(Zhou et al., 2011)	(Harrison et al., 2009)	(Serrano-Trespalacios et al., 2004)
Benzene	6.60	5.05	7.0	2.2	6.2	2.2	2.5	2.5	2.0	6.65	1.64	10.6
Toluene	28.82	24.39	59.1	19.7	23	19.7	20.8	25.1	16.3	13.07	1.53	86.1
Ethylbenzene	6.86	4.51	23.7	3.2	3.9	3.2	9.7	3.3	3.1	2.27	1.47	8.1
p-xylene	20.11	13.52	7.0	3.08	7.3	14.4	2.0	16.1	13.2	2.85	1.26	25.2
m-xylene				7.72							3.23	
Pyridine				0.25							0.15	
o-xylene	6.14	4.68	8.6	3.59	4.2					1.07	1.61	8.1
Cumene												
Dipentene												
n-propylbenzene												
Styrene				1.31	7.6	1.3	0.9	0.9	1.6	0.41	0.63	2.0
p-isopropyltoluene				1.07							0.80	
1,3,5-trimethylbenzene				0.96	1.6					0.32	0.44	
1,2,4-trimethylbenzene				3.5	1.8						1.57	
1,2,3-trimethylbenzene												
Benzaldehyde												1.9
Octaldehyde												
2-ethyl-1-hexanol												
Naphthalene				0.74		0.7	0.7	0.8	0.7		0.53	

1.2.5 Black carbon

Black carbon (BC) has been defined as the product of an incomplete combustion which contain carbonaceous residues and have because its characteristics is a light absorbing aerosol in the atmosphere (Apte et al., 2011, Huang et al., 2012b) resulting in a climate change effect (Baron Robert et al., 2011).

Major sources of BC include vehicular exhaust emissions, work and home tools that run on with fuel, residential burning, power stations, field burning of agricultural wastes, as well as forest and vegetation fires. Cooking is reported to be the main indoor source (Apte et al., 2011, Herich et al., 2011, Raju et al., 2011, Wallace et al., 2011, Dons et al., 2012, WHO, 2012, Buonanno et al., 2013b, Gramsch et al., 2013, Van Vliet et al., 2013)

Different BC measurement has been taken in personal exposure, microenvironments and outdoor sites. Because the main source of BC is the combustion, many studies have been related with traffic or in-vehicle, where higher concentrations has been obtained for India and UK (Table I-19) (Suglia et al., 2008b, Lee et al., 2010, Apte et al., 2011, Gramsch et al., 2013, Song et al., 2013, Takahama et al., 2013). Similarly, the effect of urban, semi urban, rural areas has been considered. For instance, China displayed the higher VOC values considering the spatial factor (Hitzenberger and Tohno, 2001, Dotse et al., 2012, Doumbia et al., 2012). Furthermore seasonal variation of BC concentrations has also been registered by researchers, result do not show any specific trend for BC (Allen et al., 1999, Jung et al., 2010, Herich et al., 2011, Raju et al., 2011).

Significantly emphasis has been focus on the personal exposure levels, (Dons et al., 2012, Van Vliet et al., 2013) including cycling (Liang et al., 2010), transport (Dons et

al., 2012), cooking style which has been recognized as the main source at indoors (Rehman et al., 2011, Buonanno et al., 2013a, Van Vliet et al., 2013)..

Even that most of the BC health's outcomes normally are obtained by indirect analysis using the PM, relationship between the long term BC exposure and cardiopulmonary mortality has been evidenced. Exposure to BC can lead with a decrease of cognitive functions that may affect the memory. The inhalation of BC can inflame the airways (Highwood and Kinnersley, 2006, Suglia et al., 2008b, Janssen et al., 2011, WHO, 2012, Cornell et al., 2012, Jung et al., 2012).

Table I-19 BC concentration reported in the literature (μg m^{-3})

reference	Instrument	place	Traffic		Location		Personal E		Microenvironments						season	
Characteristics			**Busy road**	**Back ground rd.**	**Urban**	**Rural**	**child**	**adult**	**cook**	**transport**	**work**	**leisure**	**home**	**shops**	**winter**	**summer**
(Apte et al., 2011)	AE-51	India	14							43						
(Buonanno et al., 2013b)	AE-51	Italy					5.1	1.59								
(Dons et al., 2012)	AE51	Belgium						1.5		5.1	1.07	2.5				
(Dons et al., 2011)	AE51	Belgium								6.4		1.27	1.22	2.5		
(Dotse et al., 2012)	SSR	Ghana			2.8										0.18	7.8
(Dons et al., 2013b)	AE51	Belgium	2.4	2.2		14										
(Doumbia et al., 2012)	AE	Africa													15.5	
(Gramsch et al., 2013)	SIMCA	Santiago	19.31	5.9												
(Hitzenberger and Tohno, 2001)	DRI, 2001	China			6.45	5.97										
(Huang et al., 2012b)	SP2	China			6.4	2.6										
(Jung et al., 2012)	SSR	N.Y USA					1.4									
(Lee et al., 2010)	AE16	Korea								2.5/1.6*					1.47[a]	0.89[a]
(Raju et al., 2011)	AE42	India							54/62[b]							
(Rehman et al., 2011)	AE51	India	24/39[b]													
(Song et al., 2013)	AE51	China	12.3/ 17.9[c]		8.1/ 16.1[c]	1.9/ 7.7[c]										
(Takahama et al., 2013)	AE51				1.8											
(Van Vliet et al., 2013)		Ghana	2.0					8.8	14.5							
(Delgado-Saborit, 2012)		UK	3.2					1.3	1.6/1.2[d]		2.9		0.95			

*morning/afternoon

[a] post- mooson/ pre-moonson

[b] morning/ evening

[C] summer/winter

1.2.6 Indoor behaviour of Pollutants

People spend more than the 80 percent of their time in indoor environments (Harrison et al., 2009), and therefore, it is important to characterize the living conditions in terms of air quality, temperature, humidity, and other parameters that contribute to comfort in indoor environments (Santamouris, 2013). The infiltration pathway of the pollutants can be influenced by several factors including human activity, natural forces, building characteristics (e.g. ventilation system), and meteorology (Al-Khulaifi et al., 2014, Banerjee and Annesi-Maesano, 2012, Branco et al., 2014). In terms of human activities, cooking, cleaning and smoking are the primary indoor contributors of $PM_{2.5}$, BC, VOCs and PAHs (Branco et al., 2014, Abt et al., 2000a, Custódio et al., 2014), and the absence of proper ventilation/exhaust systems can cause a build-up of pollutants in indoor environments (Branco et al., 2014, Clark et al., 2010, Lee et al., 2012). Other sources for indoor pollutants include office equipment such printers, photocopies (Tang et al., 2012, Wolkoff et al., 1993), cosmetic products (Steinemann et al., 2011, Rahman and Kim, 2014) spray products (Rahman and Kim, 2014) construction materials (Wolkoff, 1998, Brown et al., 1990), fire place (Hildemann et al., 1991) just to mention some. Natural forces can lead with two effects, the stack and the wind, the former is produced by the temperature differences either between indoor and outdoor or between rooms and the latter moves pollutants from areas with high pressure to lower pressure environments. These two effects influence pollutant concentration in indoor environments (Abt et al., 2000a, Al-Khulaifi et al., 2014, Custódio et al., 2014). Nowadays, a number of features, both in terms of design or technology are being implemented in buildings in order to meet the thermal comfort or the energy saving code, and this can lead positive or negative effects. For instance, more buildings are being designed with a hermetic system to keep indoor conditions

independent of the outdoor environment, which can be a positive characteristic to avoid outdoor infiltration. New chemical have also been introduced to meet new necessities in the construction, furnishing and decoration sector (Helmut K and W., 1992, Hodgson1* et al., 2000). For example, VOCs, for which primary sources include paints and vinyl and plywood flooring, are normally present during construction and redecorating process which can be controlled with appropriated ventilation (Hodgson1* et al., 2000, Liang et al., 2014). However, under certain conditions (e.g. low ventilation rates, higher indoor temperature, emission rate of product), the effect of the pollutants can be felt for a long time (Liang et al., 2014, Park and Ikeda, 2006, Armin et al., 2008).

Moreover, movement and reactions of pollutants in indoor environments differs from the outdoor. Indoor concentrations are influenced by the number and movement of people. $PM_{2.5-10}$ and VOCs have been reported to be higher during the morning and evening when activities are taking place, or during the week days (Abt et al., 2000a, Al-Khulaifi et al., 2014, Branco et al., 2014, Chithra and Shiva Nagendra, 2014, Custódio et al., 2014). Type of pollutants and their respective concentrations can also be influenced by the chemical reactions occurring between the other indoor pollutants and indoor conditions. The level of exposure can be also determined by the association that a certain compound has with other pollutants. For instance, PAHs and the oxidative form, oxy-PAHs are some of the main compounds of total carbon (TC) and TC is one of the main constituents of PM (Bandowe et al., 2014, Barrado et al., 2013, Kojima et al., 2010).

On the other hand, ambient, ground level O_3 can be formed by the reactions between pollutants in the presence of sunlight and can penetrate into buildings mostly by infiltration (Lai et al., 2015, Zhao and Stephens, 2015). In indoor environments, O_3 can

be emitted from the office equipment or be formed by the chemical reaction of VOCs with NO_x, both of which are present in indoor microenvironments (Atkinson, 2000, Demirel et al., 2014, Lee et al., 2001). The reaction of VOCs with ozone can end up in formation of second organic aerosols (SOA) which are less volatile (Chiappini et al., 2012, Civan et al., 2015, Huang et al., 2012c, Kroll and Seinfeld, 2008, Lai et al., 2015, Odum et al., 1997).

Oxy-PAHs, predominantly emitted during fuel combustion (e.g. vehicle emissions, biomass burning), and can also be formed by photochemical reaction with hydroxyl radical, which have very short lifetime and is unlikely to enter the building from outdoors (Bandowe et al., 2014, Barrado et al., 2013, Karavalakis et al., 2010, Li et al., 2015b). A majority of research studies on oxy-PAHs have focused only on outdoor microenvironments (Kojima et al., 2010, Li et al., 2015b, Ringuet et al., 2012), and insufficient information is available about indoor and personal exposure sources and concentrations, except in China (Shen et al., 2012a, Shen et al., 2012b, Shen et al., 2011, Chuang et al., 1991).

Indoor re-suspension is an important factor that can increase the indoor coarse PM concentration (Abt et al., 2000a, Branco et al., 2014, Canha et al., 2014, Chithra and Shiva Nagendra, 2014, Clougherty et al., 2011, Custódio et al., 2014). Relevant inters is around the PM as it has many constitutive such BC, PAHs, oxy-PAHs (Shrestha et al., 2010, Song et al., 2013, Takahama et al., 2013, Viana et al., 2011). PM has been considered indicator of BC risk of exposure (Wang et al., 2013b, Apte et al., 2011). According to the World Health Organization (WHO), the BC infiltration rate is higher than the observed for $PM_{2.5}$ and can vary depending on the geographical area (Jansen et al., 2005, Janssen et al., 2011).

1.3 Objectives

Thesis main objective was to characterized personal exposure (PE) to air pollutants such $PM_{2.5}$, PAHs, oxy-PAHs and BC considering several factors that influence the exposition. Therefore, four specific objectives were raised.

1.3.1 VOC concentration in new or recently redecorated houses

In indoor environments, VOCs are known to be emitted by building materials, decoration and clean products. Therefore, the FIXAT project (In quest of new **Fi**ngerprints of E**x**posure to **A**ir **T**oxics) started with the idea of monitoring the VOCs considering three different scenarios of exposure: a) subjects occupationally exposed to benzene; b) subjects living or working in new buildings (e.g. less than one year old); or building that had undergone redecoration in the previous year; and c) subjects with no occupational exposure and not living or working in new or renovated buildings (control group). Considering that the level of exposure will vary across the groups. Epidemiology studies typically use fixed site monitoring data to estimate the risk and health effects for populations. However, several studies in the existing literature conclude that the exposure levels can be under- or overestimated due to the differences in concentration between ambient, indoor and personal exposure.

The primary aim was:

> *To measure the VOC indoor concentration considering different levels of exposure allowing the identification of sources and assessment of the contribution to personal exposure in time and location. Determine the decline concentration with the time.*

1.3.2 Personal exposure vs fixed sites

Many studies have reported differences between the fixed site pollutants concentrations and indoor or personal exposure, in which main objective is to prove that the risk assessment cannot be accurately estimated by using ambient concentrations. Birmingham has sufficient information about ambient air pollutants and concentration. However, it is indispensable to identify the real subject exposure linked with the activities developed to determine the risk of exposure. This is because it has been reported that concentrations vary depending of the ambient conditions and subjects' activities and cultural behaviour. Therefore our objective was:

> *To compare the $PM_{2.5}$ concentrations between gravimetric analysis with fixed site concentration and real-time $PM_{2.5}$ monitors. Estimate the proxies with the personal and home exposure in Birmingham UK.*

1.3.3 PAH and Oxy-PAHs characterization

Special interest was in quantifying the variation in concentrations and sources of PAHs, and oxy-PAHs in typical indoor environments such as home and work, where general population spends most of the time.

The significance lies in the lack of previous reports on oxy-PAHs concentrations at the indoor and personal exposure and the carcinogenic and mutagenicity potential effect. Therefore, the main objectives were:

> *To determine the PAHs and oxy-PAHs concentration from the subject volunteers and characterize the exposure to assess the possible origin of oxy-PAHs base on the spatial and temporal variations.*

1.3.4 Black Carbon PE characterization and lung deposition

Knowing that the adverse health effects caused by the BC and considering that most of the BC is attached to the $PM_{2.5}$ particles, which deeply penetrate into the lung, the goal of this section was:

> *To monitor the temporal variations and assess source contributions of BC. Estimate the lung dose deposition considering the different subjects activities using the respiratory tract deposition model proposed by the ICRP task group.*

1.4 Thesis structure

Chapter 2 discusses methodologies used for quality control, and describes the control methods used during the monitoring, chemical analysis and data analysis.

Chapter 3 reports results from a preliminary sampling campaign (ASU-FIXAT pilot study) with the aim to identify issues with sampling instruments and the questionnaires. During this sampling period, an instrument developed by the University of Arizona was also tested.

Chapter 4 describes air quality (vis-à-vis VOCs) in recently remodelled unoccupied offices and decay rate of VOCs in new buildings.

Chapter 5 discusses the differences in VOC levels between new or recently redecorated housed and old houses. A comparison of the result of the PE with high concentration subject's exposure is also presented.

Chapter 6 reports personal, home and work exposure to $PM_{2.5}$, PAHs and oxy-PAHs.

Chapter 7 results from analysis focused on determining a correction factor for BC data, and presents results from tests focused on understanding the effect of the loading

correction and the noise reduction on the raw BC data using the recently released USEPA noise correction algorithm.

Chapter 8 discusses temporal and spatial variations of BC.

Chapter 9 discusses the formula to determine BC concentrations from Teflon filters using correlation between filter media and type of component.

Chapter 10 describes the size distribution of BC in some of the most representative microenvironments such home, office, traffic and background site.

Chapter 11 the chapter discusses methods to determine the percentage of particles sizes in each microenvironment, to subsequent split the total BC collected with the AE51 (CHAPTER VIII) in different size fractions. Also reports results related to lung dose deposition using information collected through the questionnaires and the BC size fractions (CHAPTER X).

CHAPTER II. QUALITY ASSURANCE

2.1 Sampling QA-QC

2.1.1 Blanks

During the sampling campaign, blanks were prepared to ensure the quality assurance and control. For each 10 filters conditioned and weighted, one was a blank (10%). This filter was stored in the same conditions and for the same period as the sampled filters. This was categorized as a lab blank (LB). In addition, 10% of unused conditioned sample tubes were keep in the freezer alongside with the sample tubes to be LB. Both filters and tubes were treated and analysed as samples.

Travelling blanks (TB) were clean filters and tubes that were took to the sampling sites and brought back to the laboratory. Tubes remained capped locked during the process, while filters were placed inside metal tins. Seven filters and tubes were collected as TB, which represents 10 % of the total samples.

2.1.2 Flow rates

All the pumps and the ambient instruments used were calibrated using rotameters. Rotameters were calibrated following the SOP for sampling personal exposure monitoring developed for the MATCH project, by following the instructions given in APPENDIX SOP-SAM-01 (procedure calibration of pumps using a rotameters) (Harrison et al., 2009). The rotameters were calibrated following the instruction in the APPENDIX SOP-SAM-01 (Procedure calibration of rotameters using the Gillian 2 Gilibrator). Additionally, Casella pumps allowed to adjust the flow rate. Therefore, apart from the measuring the flowrate with the calibrated rotameter, the internal flowrate

displayed in the pump was also registered. The flow rates were measure at the beginning and at the end of each sampling exercise to calculate the average flow rate.

2.1.3 Power supplied

To ensure the 24 hours run time, several modifications were done to the power supply of the pumps. Normally the SKC pumps run only for 12 hours. For that reason, extra batteries were collocated in the sampling briefcase to provide extra power to run for an additional 12 hours, thus ensuring 24 hours sampling. The Cassella pumps used AA batteries, which were charged before each sampling event. Although the MicroAethalometer and NO_2 pumps have internal batteries, these instruments are not able to run for a period of 24 hours. Therefore, the volunteers were requested to charge the instruments during the night or while they were indoors.

2.2 Analysis QA-QC

The quality assurance and control protocol for the analytical work was based on the QA/QC procedures described by (Harrad, 2005).

2.2.1 Limits of detection

The limits of detection (LOD), limit of quantification (LOQ) and the Instrument limit of detection (ILD) were calculated by using Eq.II-1, Eq.II-2 and Eq.II-3 respectively. The blank filters (7 filters and 7 tubes) which were taken from the original container were injected with the internal standard and extracted. The replica test samples results were analysed and integrated. The target analyte concentration was used to calculate the standard deviation of the replicas and multiplied by 3 to obtain the LOD.

Eq. II-1

$$\boldsymbol{LOD = 3\,SD}$$

The limit of quantification was calculated to inform the lowest concentration able to be reliably quantified by multiplying the standard deviation of the concentrations measured in the blank filters and tubes by 10.

Eq. II-2

$$\boldsymbol{LOQ = 10SD}$$

The Instrument detection limit (IDL) was calculated to determine the amount of analyte required to deliver a signal distinguishable from the background level fluctuations (Wells et al 2011). It was assessed by the noise contribution (level) of the lowest concentrations. For this purpose the standard concentration used was 50 pg μl^{-1}. The results of the IDL were given in pg $injection^{-1}$ using the following formula.

Eq. II-3

$$\boldsymbol{ILD = concentration\ of\ the\ standard * \frac{3}{signal\ to\ noise\ ratio\ of\ the\ compound}}$$

2.2.2 Blanks

Laboratory blanks were 10 % of the analysed samples. These were extracted and analysed following the same conditions as the subjects' samples. A blank was analysed at the beginning of each batch of PAH, oxy-PAH and VOC samples. These were used to test the instrument and the method performance.

2.2.3 Standard check

During the analysis, a standard check was performed to determine the adequate functionality of the GC-MS and extraction procedure. The standard was a mix of natural and deuterated PAH and oxy-PAHs compounds. The mixture was injected into a clean filter and extracted alongside the samples. For the VOCs, the standard was injected in a clean tube. A check standard was deployed at the beginning and end of each batch

of ten field tubes. For the filters, the batches were slightly large so the standard check was placed approximately after 20 subject samples following the same pattern as the tubes, at the beginning and end of the batch.

During the GC-MS analysis, a standard with knowing concentration was injected directly into the GC (no extraction process) and was placed at the beginning of each set of samples, followed by a blank and the standard extracted. Another direct standard was deployed at the end of the batch. The main objective with the direct standard was to check the performance of the instrument by comparing the known amount injected with the results obtained.

2.2.4 Calibration

To ensure that the obtained concentrations from samples were accurate, a five point calibration exercise was conducted. The target concentrations for calibration were 20, 50, 200, 500 and 1000 pg μL^{-1} for PAHs and oxy-PAHs. While for VOCs two calibration curves were performed, one for the subjects in groups with higher possible exposure (working where VOC sources presents) and for subjects with lower expected exposure. For subjects samples with lower expected concentration, the calibration points were the following 10, 50, 100, 200 and 500 ng and 100, 500, 1000, 5000 and 10,000 ng of mass for group high exposure. The primary purpose was to ensure the sensitivity, linearity and reproducibility of the instrument. The retention time and target ions were set up with the standards. The calibration process was performed every time after GC-MS maintenance was conducted.

To assess the analyte concentration in the samples, the relationship between the peak area of the analyte and the internal standard were plotted for each compound of interest. A linear regression was applied and the R^2 values were calculated.

2.2.5 Precision

The precision was computed to determine the relevance of the replica samples. The standard deviation and the mean from the replicas were used to calculate precision. For PAHs, oxy-PAHs and VOCs the precision was calculated from replica blanks, standard solution injected directly to the GC-MS, standard spiked in the filter or tube for extraction and standard reference material (NIST SMR 1649b) for PAHs and oxy-PAHs. Precision was calculated using Eq. II-4:

Eq. II-4

$$\boldsymbol{P = 100 * \frac{\sigma_{n-1}}{Mean}}$$

2.2.6 Accuracy

The accuracy defined as the bias from the true value was calculated to assure the degree of veracity in the extraction and in the analysis method. For the PAHs, oxy-PAHs and VOCs, accuracy was estimated using known values of natural standard spiked in the filters or tubes. The formula used to compute the accuracy was:

Eq. II-5

$$\boldsymbol{Accuracy = \frac{concentration\ obtained - known\ cocentration}{known\ cocentration} * 100}$$

2.2.7 Recovery of internal standard

To ensure the accuracy of the extraction, the samples were injected with internal standard before extraction, and the response of the deuterated standards was monitored. Percentage recovery was calculated using Eq. II-6:

Eq. II-6

$$\%\ IS\ recovery = \left(\frac{A_{IS}}{A_{RDS}}\right)_{S} \times \left(\frac{A_{RDS}}{A_{IS}}\right)_{STD} * 100$$

2.2.8 Standard reference material

To evaluate the analytical methods, a Standard Reference Material (SRM) certificate was analysed (urban dust SRM1649b). A total of 11 reference samples of ± 1 g of the SRM dust was extracted and analysed.

The certified concentration values are provided by the NIST (National Institute of Standards and Technology). The NIST concentration values are highly confident as bias and accuracy of the SRM have been proved. The Reference Concentration Values are the best assessment of the true values; however, these values given by NIST do not meet the criteria for the certification of the SRM as Certified Reference concentrations (EPA, 2009).

2.3 Results

2.3.1 Flow calibration

The flow rate of the pumps was calibrated before and after the sampling period by using a rotameter. In addition, the record of internal flowrate displayed in the Casella pumps was also recorded. Good correlation was observed between the internal flowrate sensor from the Micro PEM and the measurements conducted with the external calibrated rotameters (R^2=0.92).

2.3.2 Limits of detection

$PM_{2.5}$

To ensure the accuracy of the $PM_{2.5}$ weight, positive and negative measures were recorded and used to calculate the average mass. Blank filters were weighed during the pre and post sampling phases. The limit of detection and quantification were 3 µg m^{-3} and 11 µg m^{-3} respectively.

PAHs and Oxy-PAHs

Filters were treated (extracted and analysed) as subjects filter samples. The ILD was calculated for all the compounds and mostly to identify the lowest values for those compounds reported as not detectable samples (ND). The limits of detection (LOD) for PAHs and oxy-PAHs were calculated from seven clean filters which were used directly from the original container (not conditioned).

Table II-1 PAHs and Oxy-PAHs Limit of detection and ILD in ng m^{-3} from clean filters.

Compound	Mean	SD	LOD	LOQ	ILD
Naphthalene	ND	ND	ND	ND	0.03
Acenaphthylene	0.04	0.008	0.03	0.08	0.02
Acenaphthene	0.06	0.01	0.04	0.1	0.02
Fluorene	0.08	0.03	0.1	0.3	0.02
Phenanthrene	0.4	0.1	0.3	1.1	0.01
Anthracene	ND	ND	ND	ND	0.015
Fluoranthene	0.10	0.012	0.035	0.115	0.003
Pyrene	0.14	0.06	0.2	0.6	0.003
Benzo(a)anthracene	ND	ND	ND	ND	0.02
Chrysene	ND	ND	ND	ND	0.007
Benzo(b)fluoranthene	ND	ND	ND	ND	0.03
Benzo(k)fluoranthene	ND	ND	ND	ND	0.02
Benzo(e)pyrene	ND	ND	ND	ND	0.006
Benzo(a)pyrene	ND	ND	ND	ND	0.03
Indeno(1,2,3-cd)pyrene	ND	ND	ND	ND	0.02
Dibenz(a,h)anthracene	ND	ND	ND	ND	0.06
Benzo(ghi)perylene	ND	ND	ND	ND	0.02
Coronene	ND	ND	ND	ND	0.07
1,4-Naphthoquinone	0.2	0.03	0.09	0.30	0.0007
2-methyl-1,4-naphthoquinone	0.6	0.4	1.2	4.0	0.0007
Acenaphthenequinone	ND	ND	ND	ND	0.0008
Antracenoquinone	0.8	0.09	0.3	0.89	0.001
2-methyl-anthraquinone	0.4	0.08	0.2	0.79	0.002
2,3-dimethyl-anthraquinone	0.2	0.04	0.1	0.37	0.001
Benz[a]anthracene 7,12-dione	0.8	0.12	0.4	1.19	0.001
5,12-naphthacene-quinone	ND	ND	ND	ND	0.0015

ND- not detectable

The sampling parameters used to calculate the concentration were the same of the subject samples, i.e. 24 hours at 3 L min^{-1}. Results observed in Table II-1, showed that the clean filters values were lower than the reported PAHs and oxy-PAHs values from the literature.

Hence, the LOD and LOQ values demonstrated that the method proposed to characterise PAHs and Oxy-PAHs from filters collected during personal exposure sampling was appropriate to detect the compounds of interest.

The LOD for VOCs was calculated form 10 blank tubes injected with the VOC internal standard. The sampling parameters used to calculate the concentration were the same of the subject samples, i.e. 24 hours at 40 cc min^{-1} (Table II-2). The obtained LOD for VOC measurements were lower than the indoors, outdoors, microenvironments and personal exposure concentrations reported in the literature. Hence, the LOD and LOQ values demonstrated that the method proposed to characterise VOCs from sorbent tubes collected during personal exposure sampling was appropriate to detect the compounds of interest.

Additionally, in general it can be observed that not contamination was introduced by the researcher or the lab conditions when the LOD and LOQ were calculated, as can be observed from the obtained values given in Table II-2 which were low.

2.3.3 Blank.

The lab filters (LB) for PAHs and Oxy-PAHs were clean and treated as normal samples, which were conditioned and stored in the same place and for the same time as the samples.

Table II-2 VOCs detection limits in μg m^{-3}

Compound	Mean	SD	LOD	LOQ
Benzene	0.1170	0.0291	0.0873	0.2911
Toluene	0.0950	0.2676	0.8027	2.6758
Ethylbenzene	0.0077	0.0068	0.0204	0.0679
p-Xylene	0.0028	0.0037	0.0112	0.0372
m-Xylene	0.0110	0.0085	0.0255	0.0849
Pyridine	0.0004	0.0019	0.0057	0.0189
o-Xylene	0.0053	0.0047	0.0140	0.0467
Cumene	0.0001	0.0002	0.0006	0.0021
Dipentene	0.0011	0.0043	0.0130	0.0435
n-propylbenzene	0.0013	0.0012	0.0036	0.0119
Styrene	0.0080	0.0045	0.0134	0.0447
p-Isopropyltoluene	0.0024	0.0074	0.0221	0.0737
1,3,5-Trimethylbenzene	0.00004	0.0002	0.0006	0.0019
1,2,4-Trimethylbenzene	0.0005	0.0016	0.0049	0.0162
1,2,3-Trimethylbenzene	0.0005	0.0009	0.0028	0.0093
Benzaldehyde	0.0753	0.0679	0.2036	0.6786
Octaldehyde	0.0348	0.0507	0.1520	0.5067
2-Ethyl-1-hexanol	0.0620	0.0578	0.1735	0.5782
Naphthalene	**0.0080**	**0.0047**	**0.0140**	**0.0468**

The number of filters extracted were N=8 which was approximately the 10% of the total number of samples. The sampling conditions applied to calculate the concentration was a sampling duration of 24 hours with a flow rate of 3 L min^{-1}.

For the travelling blanks (TB) seven clean filters were analysed. A filter was taken in random order to the house of a subject at the start of a sample collection and then brought back to the lab once the sampling equipment was installed in the house. The filters were stored in the freezer together with the subject's samples and analysed in the same batch with the subject's filters.

The mean PAHs concentration of the LB and TB for some compounds was higher than the concentrations reported in the literature, although the differences were marginal. In some other cases, LB and TB were similar to concentrations reported in the literature (Figure II-1) (Barrado et al., 2013, Harrison et al., 2009, Albinet et al., 2007, Jung et

al., 2014, Souza et al., 2014, Zhu et al., 2014). These results lead to further investigation. Initially, possible laboratory or travelling contaminations were considered. However, when the subject's samples were analysed, it was noticed random high values for subject's samples were also measured. This turns our attention to some possible cross contamination, which might had occurred during the sampling period while the filters were stored in the freezer. An electricity breakdown occurred on campus leaving the current filters, stored in the freezer, for few hours exposed to melting ice. In general all the filters were wrapped with foil paper, but those in the bottom of the freezer drawer were the ones that experienced a little damage, including 3 TB, 4 LB, and 5 subject samples. Just after the event a register of the damage was recorder in the lab book for further clarifications. The highest damage was for those filters already conditioned to be used in future subject sampling, which were immediately discarded. As a result of this incident, higher mean values were obtained from the iced-damaged blanks increasing the mean blank concentrations. Even though the majority of the subjects filters were not exposed to water, analysed TB helped to determine any possible effect on the subjects filters from the electricity breakdown or any other laboratory or field cross-contamination. Although average travelling filters concentration for some compounds were high, in comparison with previous reported concentrations, the TB concentrations do not exceed the concentrations measured in the filters collected from the subjects participating in the FIXAT study.

Concentrations of PAHs measured from TB filters were used to correct the FIXAT subject PAHs concentrations. On the contrary, for those compounds which TB

concentrations were higher than the sample concentrations, the sample concentration was considered to be below the detection limit (BDL) for those specific compounds.

Oxy-PAHs mean concentration given by the LB filter and the TB filters was almost similar. The main differences were detected in the comparison of the clean filters with the LB and TB filters, showing three different patterns. Firstly, no detectable values were measured for acenaphthoquinone and 5,12-naphtthacenoquinone in any of the filters.

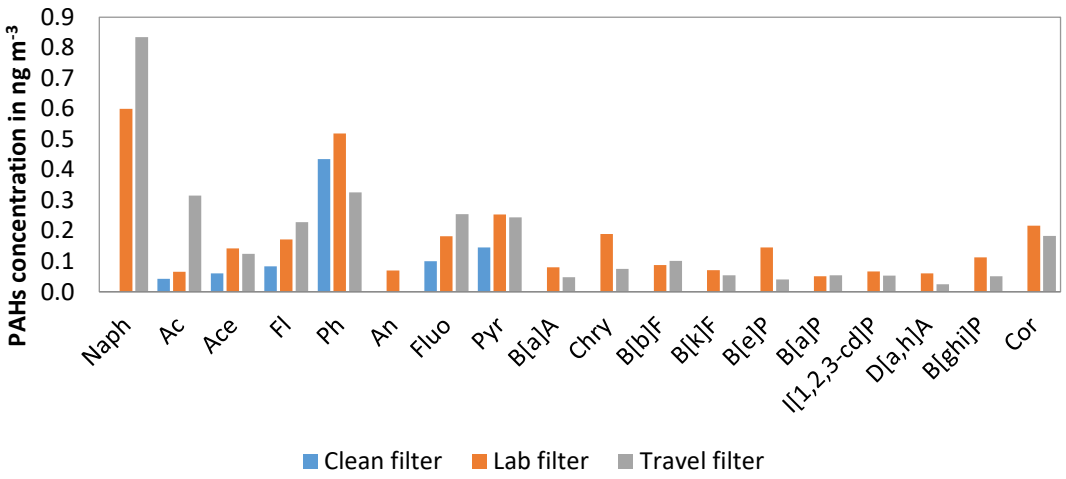


Figure II-1 PAHs mean concentration, comparison between the clean filter used to calculate the LOD, lab filter (LB) and travelling filter (TB) (ng m^{-3}).

Secondly, concentrations of the clean filter were lower than the lab and travelling filters for 2-methyl-anthraquinone and 2,3-dimethyl-anthraquinone. Thirdly, similar concentrations in the three filters were reported, such as for anthraquinone (Figure II-2).

The concentration of 9, 10 antraquinone and benzo(a)anthracene7,12-dione was higher than some of the environment concentrations reported in the literature (Delgado-Saborit et al., 2013, Albinet et al., 2007). However, it was lower than the

concentrations measured for the volunteer samples. Moreover, FIXAT samples concentrations, which include personal exposure, home and work samples, were in general higher than previous ambient samples reported for Birmingham.

Concentrations of oxy-PAHs measured from TB filters were used to correct the FIXAT subject oxy-PAHs concentrations. Those compounds which TB concentrations were higher than the sample concentrations, the sample concentration was considered to be below the detection limit (BDL) for those specific compounds.

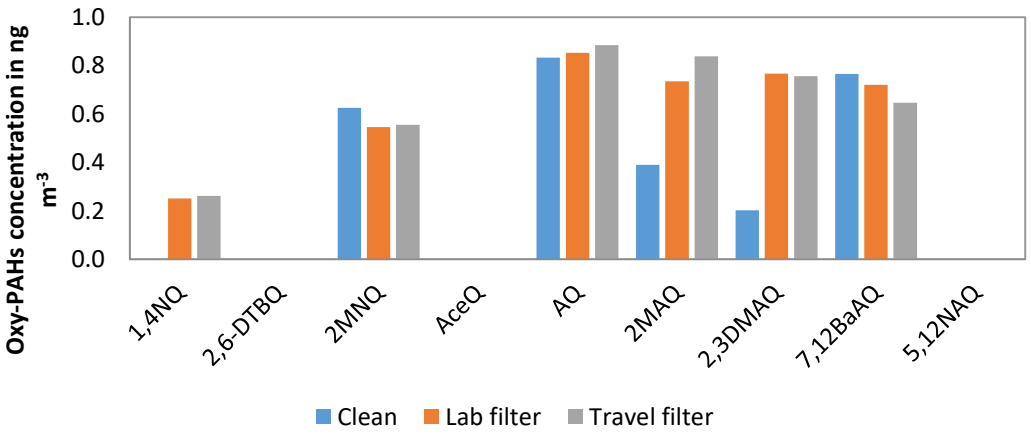


Figure II-2 Oxy-PAHs mean concentration, comparison between the clean filter used to calculate LOD, lab filter (LB) and travelling filter (TB) (ng m^{-3}).

VOC LB tubes concentration (Figure II-3) was similar to the clean tubes used to calculate the LOD. The mean concentration of each compound does not exceed the reported ambient values reported in literature. Even though, the TB tube mean concentration was higher than the clean and LB tube, the concentration is still lower than the reported in the literature. 3-vinylpyridine concentrations were deleted from the graph, for visual interpretation, as the values were higher than the average VOC blank values, reporting mean concentrations of 2.34 µg m^{-3}. Despite 3-vinylpyridine been a good indicator of ETS exposure, concentrations measured were excluded from the set

of analyses as measured values were consistently higher that previous reported concentrations, indicating a potential problem with the peak identification.

After inspection of the concentrations from all types of blanks collected, volunteers' subject concentrations were corrected by extracting the travelling blank concentration for each compound, consistent with the practice applied to PAHs and oxy-PAH concentrations. Although VOC TB tubes reported the highest concentrations, these do not exceed the ambient literature reported concentrations.

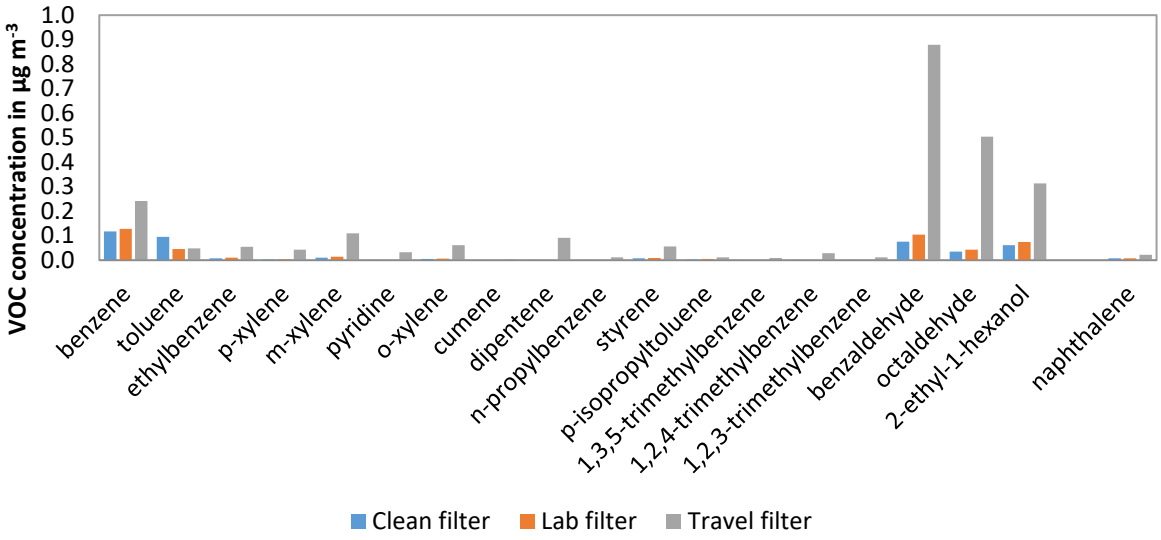


Figure II-3 VOCs mean concentration, comparison between the clean tubes used to calculate LOD, lab tubes (LB) and travelling tubes (TB) (µg m^{-3}).

Overall, the analysis of the clean, laboratory and travel blanks helped to identify some laboratory and field cross-contamination. Measures taken for the three groups of compounds are consistent. Quality measures entail to subtract the value of the travel blank to the concentrations measured in the subject samples. In addition, for those compounds which travel blank concentrations were higher than the compound concentrations measured in the sample, the concentrations of such compounds were

considered to be below the limit of detection for that specific sample. Hence, although the instrumental limit of detection was consistently low, as discussed in the section “Limits of detection”, the overall and effective limit of detection for the method was indeed defined by the threshold defined by the travel blank.

2.3.4 Precision and accuracy

PAHs and Oxy PAHS

To test the performance of the GC-MS, a standard with known concentration (200 pg μl^{-1}) of natural and deuterated compounds was analysed. The standard was placed at the beginning of each batch of samples (injected standard). And to monitor the quality of the extraction, seven clean filters were injected with a known concentration of PAHs and oxy-PAHs (50 µl) and extracted (Table II-3).

For PAHs, the performance of the GC-MS instruments was measured by calculating the precision of the method which was 8.0±1.9 % (AM±STD). The compounds which achieved poor precision (high values) were phenanthrene, which could be associated to separation deficient chromatographic separation between phenanthrene and anthracene. The peaks of benzo(b)fluoranthene, benzo(k)fluoranthene were also merging, which may have caused the low precision.

To calculate the accuracy a known concentration of 200 pg μl^{-1} was used. The results show an acceptable accuracy for all the PAHs. However for naphthalene the value was higher than the rest of the compound showing poor accuracy.

For oxy-PAHs, the concentration injected into the GC-MS was 200 pg μl^{-1}. The average precision of the oxy-PAHs method was 13±14% (AM±STD). High variations (poor precision) were registered for 5,12-naphthacene-quinone, acenaphthenequinone and

benz[a]anthracene7,12-dione with 50, 23 and 24 % respectively. For the rest of the compounds, the precision was acceptable. The bias values reported for oxy-PAHs show poor accuracy for acenaphthenequinone (-31 %), while over estimation was detectable in benzo[a]anthracene7,12-dione (16 %) and 5,12-naphthacenequinone (31 %).

Precision and accuracy values should be ± 25 % for precision and ± 20 % for accuracy. The PAHs and oxy-PAHs precision and accuracy obtained in this method are in agreement with the values reported by the EPA, except for acenaphthenequinone and 5,12-naphthacene-quinone. Which values were higher than previous reported concentrations in the literature.

The extraction method shows a clean and precise extraction for PAHs. However, high values (poor precision) are particularly observed in compounds such as naphthalene, phenanthrene and chrysene. Overall, the average precision was 12.2 %.

Respect to the Oxy-PAHs, they disclose low values for the precision (i.e. high precision), with most of the compounds having a precision value below 20%. However, the accuracy was not too good for compound such as acenaphthenequinone (-57%), Benz[a]anthracene7,12-dione (24%) and 5,12-naphthacene-quinone (32%), which consistently were overestimated; while acenaphthenequinone (-57%) was underestimated.

Table II-3 PAHs and oxy-PAHs concentration, precision and accuracy of the standard.

	Injected directly to the GC-MS				Injected and extracted from the filter			
Standard compound	Mean (pg μl^{-1})	SD (pg μl^{-1})	Precision (%)	Accuracy (%)	Mean (pg μl^{-1})	STD (pg μl^{-1})	Precision (%)	Accuracy (%)
Naphthalene	213	20	9	-7	239	34	14	-20
Acenaphthylene	196	13	6	2	202	9	5	-1
Acenaphthene	203	14	7	-1	209	11	5	-4
Fluorene	203	11	5	-2	203	13	7	-2
Phenanthrene	210	21	10	-5	241	35	15	-20
Anthracene	197	10	5	2	199	9	5	0.4
Fluoranthene	200	17	9	0	219	12	5	-9
Pyrene	201	19	9	-1	217	15	7	-9
Benzo(a)anthracene	200	15	8	0	205	9	5	-3
Chrysene	206	15	7	-3	221	15	7	-11
Benzo(b)fluoranthene	201	22	11	-1	205	15	8	-2
Benzo(k)fluoranthene	192	21	11	4	204	13	7	-2
Benzo(e)pyrene	201	14	7	-1	209	6	3	-5
Benzo(a)pyrene	197	15	8	2	203	13	7	-2
Indeno(1,2,3-cd)pyrene	197	18	9	2	203	8	4	-1
Dibenz(a,h)anthracene	197	21	11	2	206	24	12	-3
Benzo(ghi)perylene	197	14	7	2	206	10	5	-3
Coronene	207	9	4	-4	208	4	2	-4
1,4-Naphthoquinone	210	14	7	-1	217	18	9	2
2-methyl-1,4-naphthoquinone	200	15	7	-2	211	4	2	4
Acenaphthenequinone	141	32	23		87	13	15	-57
9,10 anthraquinone	205	13	7	-3	237	4	2	12
2-methyl-anthraquinone	199	19	10	-5	219	11	5	5
2,3-dimethyl-anthraquinone	210	25	12	2	237	13	6	15
Benz[a]anthracene 7,12-dione	250	61	24	17	267	52	20	24
5,12-naphthacene-quinone	273	137	50	31	274	21	8	32

VOCs

To calculate the VOC precision and accuracy, a known amount of the standard B (50 ng) was injected in a clean tube (14 tubes). The results shows that compounds like, octaldehyde and 2-ethyl-1-hexanol had poor precision and accuracy. However most of the compounds show good precision and accuracy (Table II-4).

Overall, the results of precision and accuracy highlight which compounds are characterised by the method to a higher degree of confidence, and which other compounds, mostly oxy-PAHs, octaldehyde and 2-ethyl-1-hexanol, have to be interpreted with caution.

Table II-4 VOC mass results from the standard B (50 ng)

Compound	Mean	SD	Precision	Accuracy
n-hexane	46	17	36	-8
Benzene	59	8	14	18
Toluene	47	2	4	-6
Ethylbenzene	54	2	4	7
p-xylene	52	2	3	3
m-xylene	53	2	3	6
Pyridine	55	9	16	10
o-xylene	56	2	4	12
Cumene	56	2	4	12
Dipentene	50	3	5	1
n-propylbenzene	55	3	5	10
Styrene	52	2	3	4
p-isopropyltoluene	57	3	6	14
1,3,5-trimethylbenzene	54	2	4	9
1,2,4-trimethylbenzene	55	2	4	10
1,2,3-trimethylbenzene	52	2	3	3
Benzaldehyde	54	6	11	8
Octaldehyde	59	16	27	18
2-ethyl-1-hexanol	67	15	23	35
Naphthalene	107	4	4	7

2.3.5 Calibration

According to the results, PAHs calibrations show a strong correlation between the analytical response and the analyte concentration, with average R^2 values of 0.99. The linearity of Oxy-PAHs points was less accurate as the R^2 values obtained in the regression were between 0.95 and 0.98 (Appendix 1).

For VOCs, the calibration tubes were injected with the internal standards (500 ng) and the specific concentration level of the natural standards (Appendix 2). Five calibration points were analyzed. A total of seven runs of calibration were used to determinate the points.

According to the results all the compound meet the criteria as most of them had a R^2 values close to one, the lower R^2 registered was in pyridine (R^2 =0.85). The calibration points used for all the compounds can be observed in Table II-5.

Table II-5 Calibration points for PAH, oxy-PAHs and VOC

Calibration points	VOC (ng)	PAHs and oxy-PAHs (pg m^{-3})
A	10	20
B	50	50
C	100	200
D	200	500
E	500	1000

2.3.6 Recovery of internal standard

The recovery of the deuterated compound shows an average recovery of 87±20 % (AM±SD) while the average geometric mean is 83 %. The higher variations were on compound such as Acenaphthylene, Acenaphthene, Benzo(ghi)perylene and Corone.

However the obtained values are close to those achieved by Delgado-Saborit et al., (2013). Oxy-PAHs recoveries were 61±11% and were lower than those reported by Shen et al.,(2012a), which values range from 82 ± 26 to 125±10 % (AM±SD). However, the obtained recoveries are similar to those reported by Albinet et al (2006), which fluctuated from 5 to 83 % .

The calculation of the percentage recoveries were used to assure the consistency of the extraction method. However, no correction factor derived from the calculated recoveries was applied to the CG-MS results obtained from the samples.

2.3.7 Standard Reference Material

The NIST, in the standard reference material (Urban Dust SRM 1649b) report two different concentration values: the Reference concentration values (RCV) and the certificated concentration values (CCV).

The RCVs were calculated by using PFE (Pressurized-fluid extraction) at 100˚C and Soxhlet extraction. However, in the same document values for RCV using the PFE at 200˚C were reported. The mass fraction for some of the compounds is higher when higher temperatures are applied. The Urban Dust SRM 1649b comes with moisture of 1 %. Therefore, mass values must be corrected to the 1 % of moisture. In Table II-6 we compare the values given by the NIST with the values obtained from 10 samples extracted in the FIXAT project.

The paired t-test comparison between the reference concentrations of the PFE @ 100° and the obtained concentration show not statistical difference (pair t-test $p>0.05$). The PEF @200° reported concentration were also statistical similar to the obtained concentrations (Table II-5).

Table II-6 Certificated and reference concentration (mg kg^{-1}) for PAHs reported by the NIST.

Compound	PFE at 100˚C		PFE at 200˚C		FIXAT		(Delgado-Saborit et al., 2013)
	Mean[(a)]	SD[(b)]	Mean[(a)]	SD[(b)]	Mean[(C)]	SD	Mean
Acenaphthylene	0.2*	0.04*	0.6*	0.04*	0.4	0.1	0.2
Acenaphthene	0.2*	0.03*			0.3	0.07	0.2
Fluorene	0.2*	0.02*	0.3*	0.003*	0.3	0.04	0.2
Phenanthrene	4	0.05			4	0.7	4.0
Anthracene	0.4*	0.002*	0.9*	0.04*	0.6	0.13	0.4
Fluoranthene	6.1	0.1			6.1	1.2	6.0
Pyrene	4.8	0.03			5.2	1	5.0
Benzo(a)anthracene	2.1	0.05			2	0.9	2.1
Chrysene	3.008	0.04			4.6	0.6	3.1
Benzo(b)fluoranthene	6	0.2			5.8	0.5	5.8
Benzo(k)fluoranthene	2	0.08			3.3	0.6	2.2*
Benzo(e)pyrene	3	0.04			3.3	0.4	2.7
Benzo(a)pyrene	2	0.2			2.6	0.5	2.4
Indeno(1,2,3-cd)pyrene	3	0.2			3	0.4	3.0
Dibenz(a,h)anthracene	0.3	0.004			0.6	0.1	0.3
Benzo(ghi)perylene	4	0.05			4.2	0.5	3.9
Coronene	3*	0.5*			4	0.3	3.0

[(a)] Mean concentration is reported as a dry-mass basis

[(b)] Reported as an expected uncertainty in which U, is calculated by $U = ku_c$ where u_c is the standard deviation and k which is the associated degree of freedom and the 95% of confidence for each analyte when the t-test distribution is applied.

[(C)] Mean concentration reported with a 1% of moisture.

* References concentration

For those compounds which NIST do not provide the reference values, the SRM report the certified values. Not statistical difference was observed between the certificated concentration reported by the NIST (SRM 1649b) and the obtained concentrations analysed by the SRM 1649b reference material dust (pair t-test $p>0.05$) (Table II-6).

For Oxy-PAHs the SRM 1649b only report values obtained from inter-laboratory studies. Comparing our results with the given values (SRM1649b) was found that the results obtained were slightly lower that the expected values (Table II-7).

However compounds such 1,4 napthoquinone concentration varies across the literature from 0.4 mg kg^{-1} reported by Delgado-Saborit et al.,(2013) to 0.240 mg kg^{-1} obtained by (Cho et al., 2004), while our value is 0.7 mg kg^{-1}. For 1,4-naphthoquinone, 9,10- anthraquinone, 2-methyl-anthraquinone, 2,3-dimethyl-anthraquinone and 5,12-naphthacene-quinone large differences can be observed between our values and those reported by Delgado-Saborit et al.,(2013).

2.4 Conclusion

Limits of detection (LD) and quantification were calculated for $PM_{2.5}$, PAHs, oxy-PAHs and VOCs. All the $PM_{2.5}$ measurements were above the LOD and LOQ.

For PAHs and oxy-PAHs and VOC, three different LOD were calculated. LOD calculated from clean blank filters (i.e. filters taken from the original container), showed good results with very low values, indicating that the researcher was proficient in the analytical technique.

Analysis of the laboratory and travel blank, in comparison with the clean blank filters suggested that some cross-contamination occurred in the field or the laboratory. Further investigations were conducted to elucidate the cause, which suggested to be related to an electrical breakdown affecting the laboratory freezers where samples were stored. Hence, concentrations measured from travel blanks were used to correct (i.e. subtract from) the FIXAT subject concentrations. Those compounds which travel blank concentrations were higher than the sample concentrations, the sample concentration was considered to be below the detection limit for those specific compounds.

Table II-7 Values given by the NIST for some of the Oxy-PAHs (mg kg^{-1}).

		FIXAT		SRM1649b	(Delgado-Saborit et al., 2013)	(Albinet, 2006 #420)	(Cho, 2004 #161)
Compounds	**Mean[(C)]**	**SD**	**Precision**	**Mean[(a)]**	**Mean**	**Mean**	**mean**
1,4-Naphthoquinone	0.7	0.1	16.1		0.4		0.24
2,6-di-tert-butyl-1,4-benzoquinone	0.1	7.5	72.5		0.09		
2-methyl-1,4-naphthoquinone	1.6	0.2	12.6		0.3		
Acenaphthenequinone	1.7	0.2	12.3	1.8	1.8		
9,10- anthraquinone	3.01	0.4	14.1		3.0	2.23	2.03
2-methyl-anthraquinone	2.4	0.3	14.3		0.4		
2,3-dimethyl-anthraquinone	2.0	0.4	20.2	3.6	0.1		
Benz[a]anthracene 7,12-dione	4.7	0.8	16.0		3.4	8.45	
5,12-naphthacene-quinone	8.6	1.0	11.0		2.8		

[(a)] Mean concentration is reported as a dry-mass basis
[(C)] Mean concentration reported with a 1 % of moisture.

This decision might underestimate the obtained concentration from subject's samples However, considering the results obtained from the FIXAT volunteers, the values were similar to previous samples taken in Birmingham or even higher (see chapter V for references).

The results of precision, accuracy and reference standard materials provide a high degree of confidence for the results reported for PAHs and VOCs, whilst show lower confidence for concentrations characterised for most oxy-PAHs.

To sum up, a thorough quality assurance and quality control protocol has been implemented to ensure that the analytical methods proposed were suitable to characterise the concentrations of PAHs, oxy-PAHs and VOCs in samples collected from personal exposure, home and work microenvironments. In addition, blanks measurements have helped to identify cross-contamination occurred in the laboratory or field and correct accordingly the concentrations analysed. The values of precision, accuracy and comparison with reference standards provide information on the range of compounds that can be characterised with confidence, such as PAHs and VOCs, whilst other compounds (mostly oxy-PAHs) show a lower degree of confidence in the reported concentrations.

CHAPTER III. ASU-FIXAT PILOT PROJECT

3.1 Introduction

Quantification of air pollutant concentrations in indoor and outdoor environments is not a reliable estimation of the personal exposure (PE) to the pollutants, and several studies have highlighted a lack of correlation between ambient and PE concentrations (Du et al., 2010, Borgini et al., 2011, Delgado-Saborit et al., 2011a, Meng et al., 2012, Michikawa et al., 2014). Much of the research in this field has been conducted using time-integrated samples, and although such samples can provide good information for the PE over a specific duration of time, the information is often subjective. This is because even though it is possible to estimate the sources based on previous information reported, concentrations can vary and are influenced by several factors such as temperature, humidity, location, activity, etc. In line with developments in the field, new technology and methods are also being developed to enhance instrument portability and characterize the PE properly (Buonanno et al., 2014). Online instruments allow tracking of air pollutant concentrations in real time, which can be correlated with locations and activities reported by the subjects (Chen et al., 2012).

At the personal level, VOCs are normally sampled by using sorbent tubes mounted on pump to then be desorbed thermally and analysed by using the GC-MS, which is the most common technique (Fischer et al., 2000, Jo and Kim, 2010, Sofuoglu et al., 2010, Delgado-Saborit et al., 2011a, Kliucininkas et al., 2011, Lehtinen et al., 2013, de Gennaro et al., 2014, Rahman and Kim, 2014). However, several studies have used passive samples as they are easy to handle, as energy is not required and the extraction is by

using solvent desorption (Guo et al., 2009, Johnson et al., 2010). Another method to collect air samples is by using canisters (Ho et al., 2002, Guo et al., 2004, Ho et al., 2004, Stocco et al., 2008, Zhou et al., 2011, Weichenthal et al., 2012, Zhu et al., 2013a). All the above-mentioned methods collect an integrated sample given at the end the concentrations per selected compound in a period. However, nowadays online equipment, that collect continuous samples of VOC, have also been used to characterize VOCs, given real-time results, but making unavailable the compound concentration.

On the other hand, BC can be obtained by measuring the combustion products (CO_2) or by quantifying the absorption. BC concentrations initially were calculated from the $PM_{2.5}$ concentrations by dividing the carbonaceous material in EC and OC, elemental and organic carbon respectively. This method is considered the thermal technique (EC data), while the optical method results in BC concentration (Hansen et al., 1984, Hitzenberger et al., 1999). However, both are considered to be the result of the incomplete combustion which results can be comparable (Lavanchy et al., 1999, Hitzenberger and Tohno, 2001). The Aethalometer™ is the leading instrument for real-time measurement of optically-absorbing 'Black' or 'Elemental' carbon aerosol particles (Park et al., 2010). MicroAeth™ Model AE51 is the miniature real-time monitor for Aerosol Black Carbon. The MicroAeth incorporates the same Aethalometer® measurement technology, but packages it in a way that the instrument can fit in the pocket (AethLabs, 2012). ASU- pilot project was run before to sample the FIXAT subjects. The main FIXAT objective was to sample three different levels of VOC exposure, and characterize their activities by using different types of questionnaires. Because the conventional VOC lab methodology was planned to be

used, and leveraging the opportunity of the Arizona State University, that gave the team to test the new developed sensor; the main objective was to test both methodologies. Therefore, a pilot study was focused on the validation of a new sensor developed by the Centre of Bioelectronics and Biosensors at the Biodesign Institute, Arizona State University. The ASU's total VOC (TVOC) sensor (Chen et al., 2012), was used for the first time by the research group to characterize personal exposure. The objective was to validate the instruments by sampling general population, identify the range of concentrations of VOCs in different environments and their possible sources and estimate the difference between the online TVOCs measurement against the measurements with a conventional lab method which includes thermal desorption and GC-MS analysis. The aim of using the MicroAethalometer unit was to investigate the possible relationship between the levels of BC and VOC, and compare the results with previously reported results in the literature. Another aim was to determine the wearability of the sensors and sampling bags containing the sampling equipment that was considered being used in the FIXAT samples. Finally, to test the questionnaires that might be used in the FIXAT project.

3.1.1 ASU's TVOCs online sensor

The light weight sensor (370 g) has been developed for use as a personal sampler, and can log the data using a wireless system. The instrument consists of a detection unit composed of sample collector and conditioner, sensor array and detection circuit and a user interface; which is an smartphone that receives and refines the data from which the results can be logged (Chen et al., 2012). The sensor has been tested for stability and can be used for sample collection across a range of activities.

In general, the sensor works in 1:2 cycles, i.e. one minute of sampling followed by two minutes of purge (3 min- interval). The device works by a sensor “tuning fork” with prongs that are coated with either polymers or molecule. Depending on the target VOC and the sensing layer, the prongs will detect different properties and therefore a change in mass in the tuning will increase, producing a change in the frequencies. These frequencies can be detected by the digital circuit and send the information to the user-interface software which will show the concentration data (Tsow et al., 2009). Compounds such aromatic, alkyl and chlorinated VOCs can be measure with high sensitivity with a high resolution of 4 ppb -1 ppm. Because the VOC level varies, based on the environments and conditions, the instruments were calibrated by using dual point calibration based on the motor vehicle exhausts (MVE) and indoor air quality (IAQ) to end up with outdoor and indoor calibration points. Moreover, field tests were also include into the calibration, considering indoor remodelling, traffic exposure, and working. Then the calibration factor was calculated by computing the fractional sensitivity contribution of the compounds obtained from the mixture of environments and conditions.

3.1.2 MicroAeth (AE51)

Real-time MicroAeth model AE51, analyses BC by measuring the rate of change in absorption of transmitted light due to continuous collection of aerosol deposits on filter. Measured at 880 nm and interpreted as concentration of Black Carbon (BC). Real-time, 5-min interval data has enabled the use of the instrument for personal exposure measurements (AethLabs, 2012, Cheng and Lin, 2013).

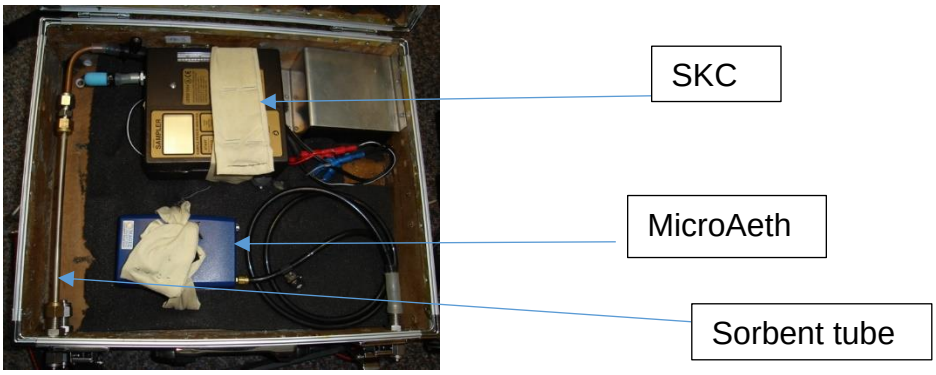
3.2 Objective

To have a preliminary sampling campaign to test instruments, sampling bags, questionnaires and possible use of equipment for FIXAT campaign and to test equipment from the University of Arizona capable of reporting online total VOC.

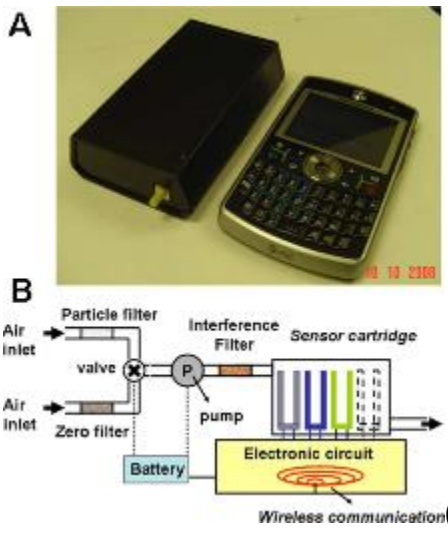
3.3 Methodology

3.3.1 Sampling

To meet the objectives in the pilot study, 10 non-smoker subjects were recruited from the University of Birmingham. Students or family member were willing to participate They were asked to carry a briefcase containing a sorbent tube connected with a SKC pump to collect integrated samples of VOCs, which were split to take eight hours during the day and second tube to take the rest of the day/night to complete 24 hours concentration (Picture III-1). The main objective was to have co-located samples of the integrated and the ASU TVOC sensor to collect the real-time TVOCs for eight hours (Picture III-2). Additionally, the BC sensor (MicroAethalometer AE51) was used to collect 24 hours samples. During the sampling campaign, volunteers were advised to continue their normal activities and were requested to fill the time-activity diary (TAD) questionnaire, in which the exact time of the activity was recorded (Appendix 3). At the end of the eighth hour sample, the tube was changed and the ASU TVOC sensor was removed to download the information and prepare it for the next volunteer.



Picture III-1 Briefcase containing the SKC pump and the microAethalometer.



(Chen et al., 2012)

Picture III-2 ASU's TVOC sensor.

Picture III-3 ASU's carry bags.

To test the wearability, subjects were asked to fill in a questionnaire which was used to characterize the comfort, weight, noise and general operation of the air sampling equipment and the sampler carry bags (Picture III-3) (Appendix 4) Volunteers were also asked to fill in the questionnaires create to FIXAT project (Appendix 5) and flag any questions that weren't clear so as to rectify the errors and validate the questionnaires.

3.3.2 Analysis

Data from the ASU TVOC sensor and MicroAethalometer was downloaded to the computer and analysed using the Microsoft Excel program and IBM SPSS V.21., while the sorbent tubes were analysed following the MATCH project SOP (Harrison et al., 2009).

Integrated samples were constituted by averaging or summing the concentration of the 20 analysed compounds by subject, while the sensor concentration was the average or sum of the total (8 hours) 3-min sampling data per volunteer. Either the subject average or accumulation concentration was used to build the dispersion graphs.

To calculate the time-weighted contribution of various microenvironments to overall PE to BC, the formula proposed by (Harrison et al., 2009) was used (Eq. III-1).

Eq. III-1

$$K = \frac{\sum_{i=1}^{I} \frac{t_{ik \times X_{ik}}}{T_i}}{\sum_{\mathrm{i=1}}^{\mathrm{K}} \sum_{i=1}^{I} \frac{t_{ik \times X_{ik}}}{T_i}} \times 100$$

Where
t_{ik} is the time spent in a microenvironment,
k by subject *i*,
X_{ik} is the average concentration of microenvironment *k* for subject *i,* and
T_i is the total time spent in all microenvironments by subject *i*.

3.4 Results and discussion

3.4.1 Comparison of TVOC concentrations from the real-time sensor and lab-based analytical method

According to the questionnaires, subjects' house location were mainly near the university, living in a flat or terrace houses, with no garage connected. The ASU sensor displayed the concentrations in ppbC, while the integrated sample in µg m^{-3}. To do the comparison, concentration expressed in µg m^{-3} was converted to ppbV and then the results were multiplied by the total number of carbons present in each compound to have the concentration at ppbC.

Since the time-integrated sample was analysed for a set of compounds, the sum (cumulative concentration) of 20 compounds per subject was used for comparison with the TVOC 3-min sum concentration per subject obtained from the VOC sensor. To determine any difference in concentrations, the average of the 20 compounds were compared with the average of the sensor readings (TVOC 3-min).

Statistical differences were reported for n-Hexane, with higher values during the day (Table III-1). Despite no observed statistical difference (independent t-test $p>0.05$) for the relationship between day and night VOC concentration of most of the compounds, higher values were registered during the night for dipentene and octaldehyde. Possible reasons might include cleaning, cooking, house work, as according to the TAD most of the time was spend at work or out of the house during the morning, therefore, high afternoon home activities were developed. High VOC concentrations have been reported for cleaning products which are the major source of indoor emission (Edwards et al., 2001).

Table III-1 VOC concentration (ppbC) analysed from the integrated samples (N=10).

	day		night	
Sampling time	8 h		16 h	
	AM	SD	AM	SD
n-hexane	4518a	2049	2851a	757
Benzene	3.15a	1.3	2.47a	0.5
Toluene	1008a	1023	1128a	713
Ethylbenzene	4.53a	6.0	3.01a	2.1
p-xylene	3.98a	6.3	1.87a	1.5
m-xylene	9.83a	14.4	4.75a	3.7
Pyridine	0.59a	0.6	0.69a	1.3
o-xylene	5.76a	8.1	2.84a	2.1
Cumene	0.43a	0.5	0.34a	0.2
Dipentene	61.4a	43.8	102a	87.7
n-propylbenzene	0.92a	1.7	0.45a	0.2
Styrene	2.89a	2.0	4.17a	2.4
p-isopropyltoluene	3.16a	1.9	7.53a	7.7
1,3,5-trimethylbenzene	1.62a	2.5	0.45a	0.3
1,2,4-trimethylbenzene	3.73a	7.1	1.56a	1.0
1,2,3-trimethylbenzene	1.17a	1.7	0.70a	0.5
Benzaldehyde	6.35a	2.7	10.5a	6.9
Octaldehyde	8.60a	3.8	15.7a	10.3
2-ethyl-1-hexanol	22.6a	13.2	26.9a	21.2
Naphthalene	1.58a	1.0	1.44a	1.3

AM- Arithmetic mean, SD- Standard deviation
Independent t-test ($p < 0.05$) has been used to test for statistically different concentrations between sampling time (day and night). No statistical difference is indicated by similar letter.

Considering the relationship between the integrated sample and online concentrations, poor correlation was observed between the average data (R^2=0.63) (Figure III-1). However, the cumulative concentration shows a better relationship (R^2=0.83) (Figure III-2). This correlation was also found in previous test of the instruments reporting a correlation coefficient higher than R^2=0.9 (Chen et al., 2012).

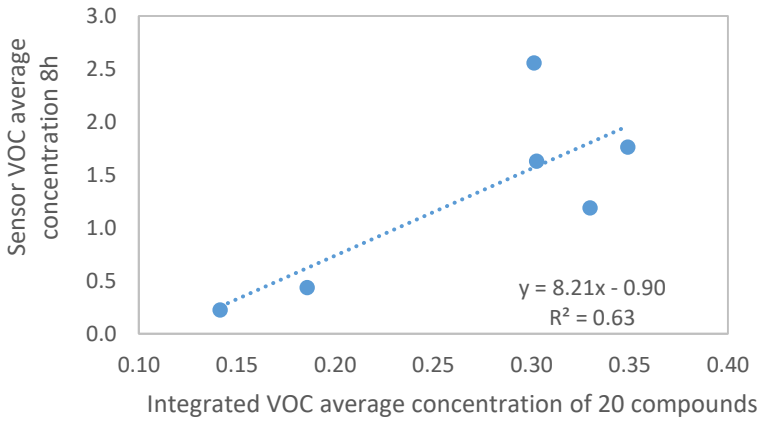


Figure III-1 VOC average concentration, relationship between online sensor (3-min) and the integrated samples form the sorbent tubes (20 compounds) obtained for a sampling period of 8h (ppmC).

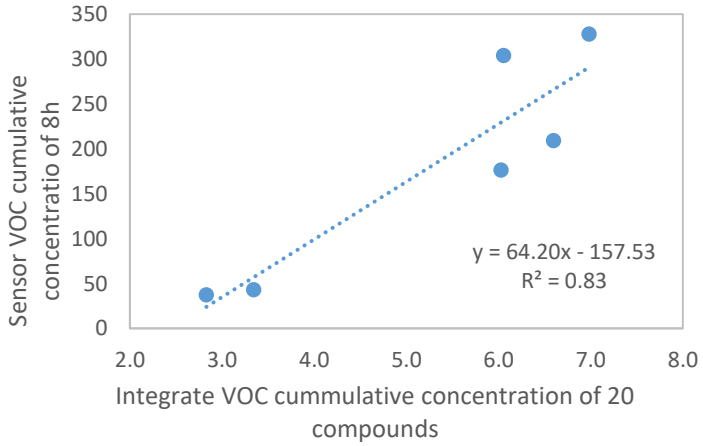


Figure III-2 VOC cumulative concentration, relationship between the online instrument (3-min) and the integrated sample from the sorbent tubes (20 compounds) obtained for a sampling period of 8h (ppmC).

Although integrated and sensor concentrations had showed a good relationship by using the average (Figure III-1) and cumulative (Figure III-2) concentrations, values from the sensor were registered to be higher than the lab. Difference in concentration might be

attributable to the sensor sensitivity as it was reported to have sensitivity to alkyl, aromatic and chlorinated hydrocarbons (Chen et al., 2012), which are known to be present in elevated concentrations in a normal environment; while using the lab method, the number of analysed compounds (20) can vary from sample-to-sample influencing the TVOC concentrations.

The correlation coefficients indicate that the sensor accounts for 63 % and 83 % of the variance in the concentration data from the adsorption tubes for the average and cumulative concentrations respectively. However, the intercept was negative on the y-axis. Therefore, positive integrated values were observed when the sensor was reading zero. By solving the regression equation for y=0, $\underline{x}$ value for the cumulative mode was 2.45, while for the average mode $\underline{x}$ was 0.10. Despite the sensor's reported detection range of 4 ppb to 1000 ppm (Chen et al., 2012), what can be observed is a problem with the differences in the limits of detections. Therefore concentrations below those values cannot accurately be predicted as negative values will be obtained.

3.4.2 VOC concentrations from the ASU sensor

Most of the subjects in the study were students (or their family members) from the University of Birmingham. From the VOC sensor, only seven subjects' samples were obtained and the sampling period using the online instruments was from 08:00 to16:00 h. Base on the TAD, during the sampling day two subjects spent most of the time at work (~ 8 hours). In general, the highest average concentration was recorded in in-transit (4.6 ppmC) and this observation is in line with previous reported VOC values for transport (Kim et al., 2001). Measurements of traffic had been obtained by using the VOC sensor

reporting concentrations of 6.43 ppmC for a high traffic road, which exceed our mean concentration (Chen et al., 2012). In-transit commute mode includes bus, car, train, and walking activities (Table III-2). The transport mode data was tested using ANOVA ($p < 0.001$), and confirmed by the Tukey test. Bus (11.89 ± 11.70 ppmC) had the highest exposure concentration (AM±SD) followed by car (4.24 ± 5.13 ppmC), walking (3.9 ± 4.30 ppmC) and train (2.24 ± 2.77 ppmC). And this can be observed in Figure III-3, in which the time series concentration per volunteer are plotted. According to (Guo et al., 2004), the risk of exposure to VOCs shows a higher average of lifetime cancer for bus riders than for those that use the railway. Home concentration (0.29 ppmC) were lower than reported ones during the sampling test campaign developed by (Chen et al., 2012). Moreover, higher concentrations were observed in other indoors places like pub (0.96 ppmC) and work (0.54 ppmC) than home, as observed in the high peaks from Figure III-3.

Table III-2 Summary of the total average of all subject activities VOC concentration (ppmC) in various categorized microenvironments over 8 h (08:00- 16:00) (N=7 subjects).

	N	Mean	SD	Time spent (min)	% time
Home	399	**0.29**	1.29	1197	34.8
Work	495	**0.54**	2.23	1485	43.1
Other indoor	69	**0.96**	2.37	207	6
In-transit	157	**4.59**	6.34	471	13.7
Bus	16	11.88a	11.70		
Car	123	4.23b	5.13		
Walk	18	3.90b	4.27		
Train	9	2.23b	2.77		
Outdoor	28	**4.23**	5.70	84	2.4

ANOVA ($p < 0.05$) has been used to test for statistically different concentrations between commute modes. No statistical difference was indicated by similar letter.

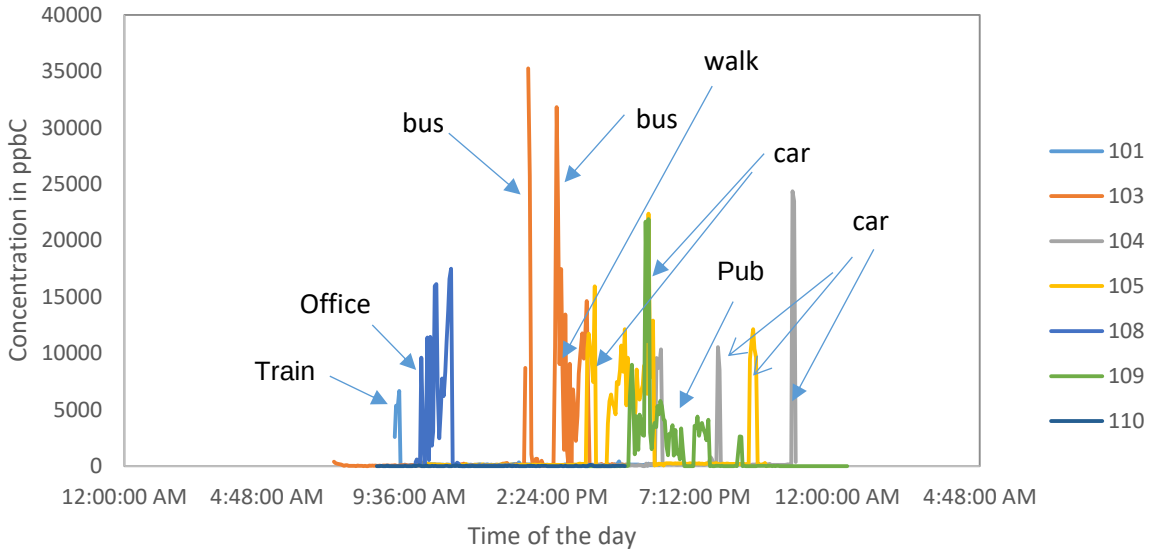


Figure III-3 TVOC concentration (ppbC) based on the ASU TVOC sensor considering only seven subjects as three samples were lost.

3.4.3 Integrated VOC concentration

Analysis of integrated VOCs in the laboratory has its advantages like the ability to characterize different compounds, being one of the foremost since it helps in source attribution. Results showed that the most abundant compounds were toluene (1008 ppbC) and dipentene (61.58 ppbC) (Table III-1). Dipentene is used as a solvent in many products because of its lemon odour, it can be found in perfumes, cleaning products, air fresheners, diapers and the compound can also infiltrate from the outdoors (Su et al., 2013, Stocco et al., 2008). Differences in day and night concentrations were observed indicating that normally subjects at this time clean or use any kind of refresh to aromatize the house. Toluene is one of the most abundant compounds in indoor environments (Wang et al., 2009, Guo et al., 2009, Rahman and Kim, 2014, Sarigiannis et al., 2011, Sofuoglu et al., 2010) and it is emitted during cooking activities (Byun et al., 2010), from photocopier

machines as it is found in printer ink (Sarkhosh et al., 2012, Yu and Jeong Tai Kim, 2010). After those compounds 2 ethyl-1 –hexanol, octaldehyde and benzaldehyde were also found to be present in high concentrations in most of the subjects' activities (Figure III-4).

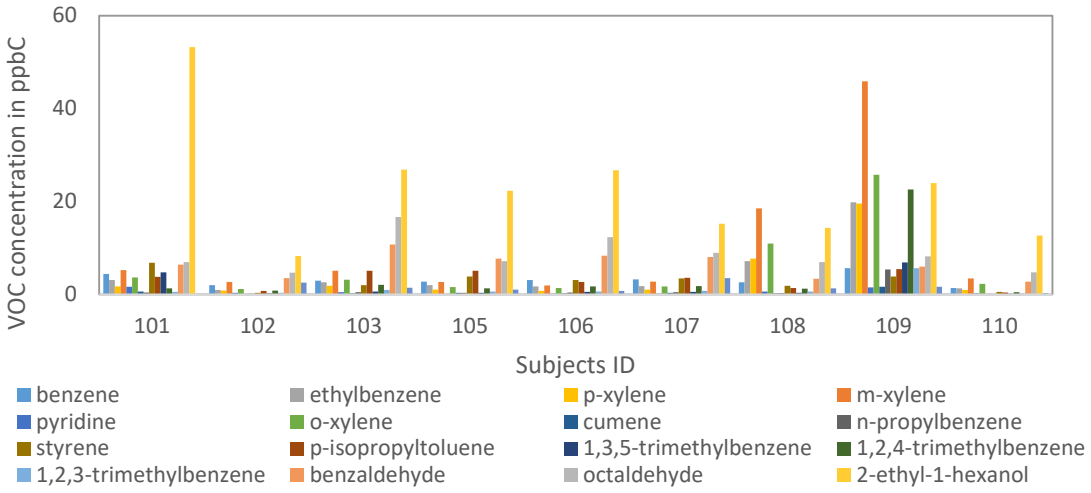


Figure III-4 VOC concentration obtained from the sorbent tubes of 8 hours sample and converted in ppbC.

3.4.4 Time-weighted contribution

Time-weighted contribution was calculated for the activity categories to determine the influence of the time of exposure concentration the percentage of exposure was also plotted. Despite that subject 101 spent most of the time developing work activities, the time-weighted contribution was higher for other indoor activities and in-transit (Figure III-5). Similar trends were observed for subjects 103, 104 and 105 with high in-transit contribution. Nevertheless subject 109 showed higher time- weighted contribution during outdoor activities (city centre) according to the TAD. During the sampling day, subjects 108 and 110 spent most of the time at the office microenvironments, therefore they had around 100 % of time-weighted contribution.

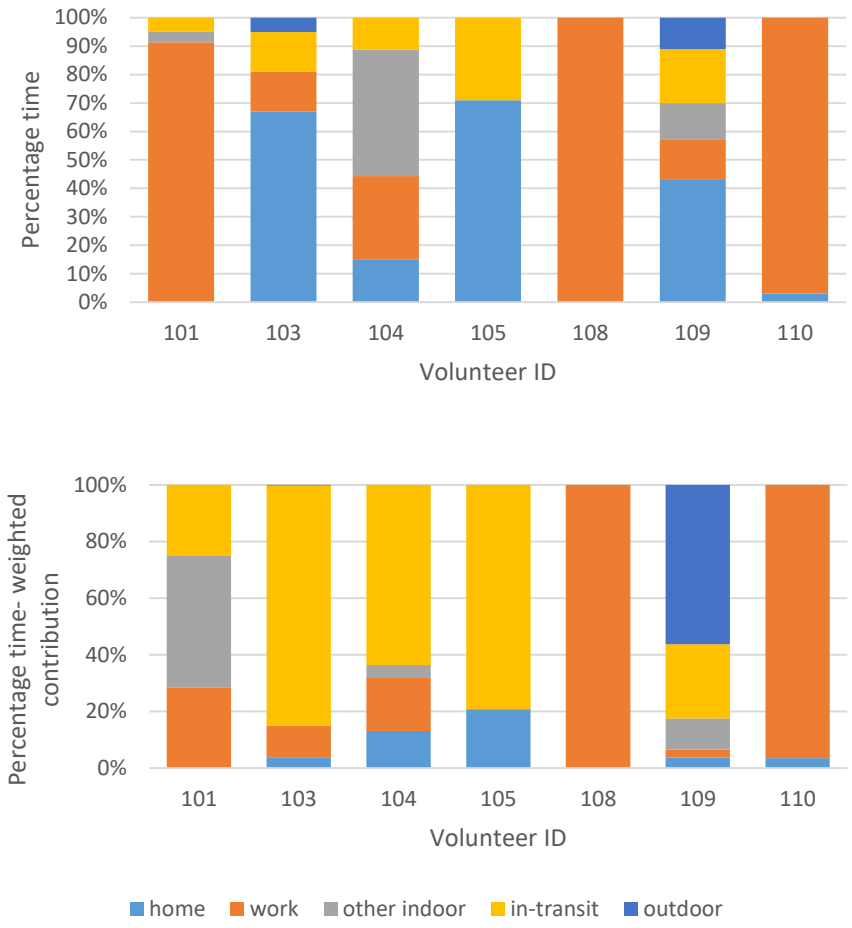


Figure III-5 VOC time- weighted contribution (sampling time= 8 hours), from 8:00 to 16:00 hours.

3.4.5 Integrated analysis

Having integrated, online concentration and the time contribution, the personal exposure can be analysed considering these three factors. For instance, subject 109 who registered high concentration of most of the compounds (Figure III-4) spent most of the time at home (Figure III-5). However, these activities were not the source of high concentration. According to the online data and the TAD, higher peaks were observed during car commute and socializing in the outdoors (pub). And this can be confirmed by the

percentage time-average contribution which is higher for outdoors. What can be observed for Figure III-4 was high combustion emission compound (BTEX), which are normally emitted from diesel or petrol (D'Souza et al., 2009, Kim et al., 2001, Wang et al., 2009). This can be attributable to high time exposure at the outdoors and the contribution of office, and in-transit, considering these two microenvironments as high contributors of BTEX exposure (Kim et al., 2001). However, in- transit BTEX concentrations were not too high as can be seen for volunteers 101, 103 and 105 (Figure III-4). But the online data suggest high concentrations during the commute mode because more compounds are taken in consideration on the online sensor. Other high compounds observed in subjects 103 and 105 were styrene and p-isopropyltoluene, and these compounds have been reported to be abundant in emissions from diesel vehicles (Tsai et al., 2012). In general, traffic has been found to be the major source of VOCs in outdoor environments (Massolo et al., 2010, McCarthy et al., 2013, Wang et al., 2013a) and the major time-average contribution percentage was observed for in-transit (Figure III-5)

Office difference can be seen in Figure III-4. Offices that face the road have higher BTEX concentration (108), while subject with no windows facing to the road had lower exposure concentration (110). Possible sources of BTEX and other VOCs at the office can be office material, equipment and cleaning products (D'Souza et al., 2009, Jo and Kim, 2010).

3.4.6 BC concentration

BC concentration was analysed based on the principal locations visited by volunteers. Results show that higher concentrations were found while subjects commute. Showing high standard deviation, which is the effect of the differences between different transport

modes (Table III-3). Result shows that car registered higher concentration compared with the other commute modes (ANOVA p>0.05).

Table III-3 BC concentrations (ng m^{-3}) obtained from the ASU- pilot project.

	N	Mean	SD	Time spent (min)	% of time
Home	130	797	254	130	26
Work	233	649	375	233	46
Other indoor	38	2484	2728	38	7
In-transit	93	4393	11766	93	18
Bus	31	1924a	1404		
Car	78	5051b	12751		
Street	32	1087a	578		
Train	6	819a	152		
Outdoor	13	944	418	13	3

ANOVA ($p < 0.05$) has been used to test for statistically different concentrations between commute modes. Not statistical difference was indicated by similar letter.

The concentrations obtained in the eight hour samples were lower than the reported by (Delgado-Saborit, 2012) for home, office and outdoor in a sampling period of 16-22 hours. BC car concentrations were higher than the obtained by (Delgado-Saborit, 2012). Considering that car also shows high standard deviation, other exposure characteristics might be considered during the sampling campaign like, car model, traffic and fuel type.

The time average contribution percentage was calculated and compared with the percentage of time exposure (Figure III-6). Despite the high time exposure at home observed for subjects 104,105 and 109, the average-time percentage contribution was much less. The higher average-time was observed for in-transit and other indoors general activities even that the exposure time was less.

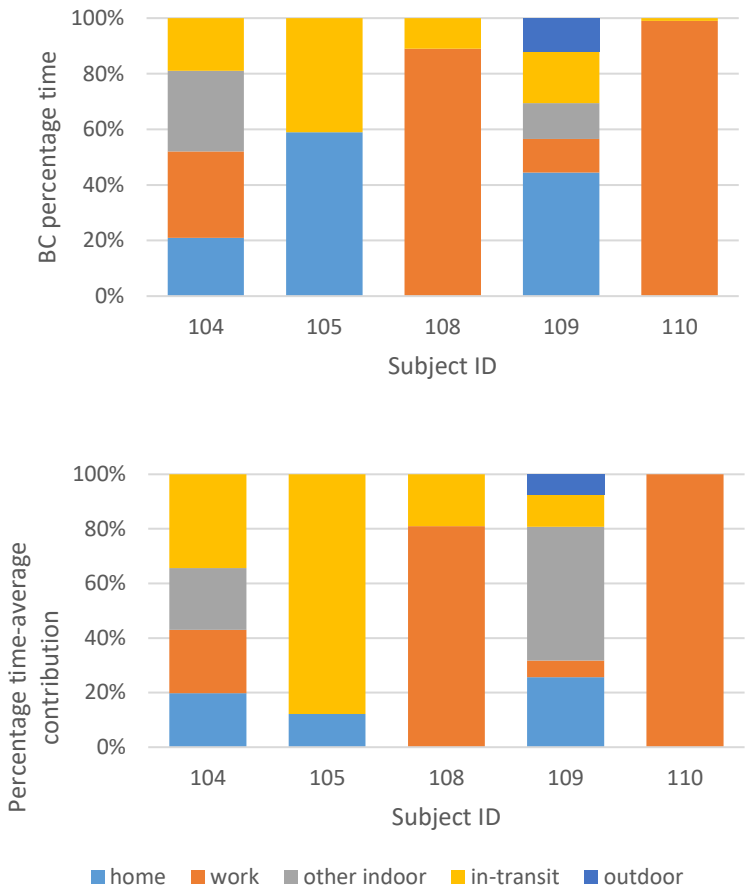


Figure III-6 BC average- time contribution calculated from the BC concentrations obtained in the ASU-pilot project.

The time series concentration can be observed in Figure III-7. The plot shows higher values during the afternoon while subjects commute or at home based activities. According to the literature, transport (car) is considered the main emission source of BC followed by home based activities (Dons et al., 2012, Delgado-Saborit, 2012, Buonanno et al., 2013b, Van Vliet et al., 2013, Cheng et al., 2014). However, high peaks were also found for leisure (e.g. shopping and entertainment activities (e.g. socializing) (Dons et al., 2011, Dons et al., 2012). The intensity of BC concentration can depend on many factors such as traffic (Dons et al., 2013a), time of the day and length of the journey. In this study,

for instance, subject 105, who had a long journey at peak traffic time shows high BC levels compared with subject 108 who had a shorted journey (Lee et al., 2010).

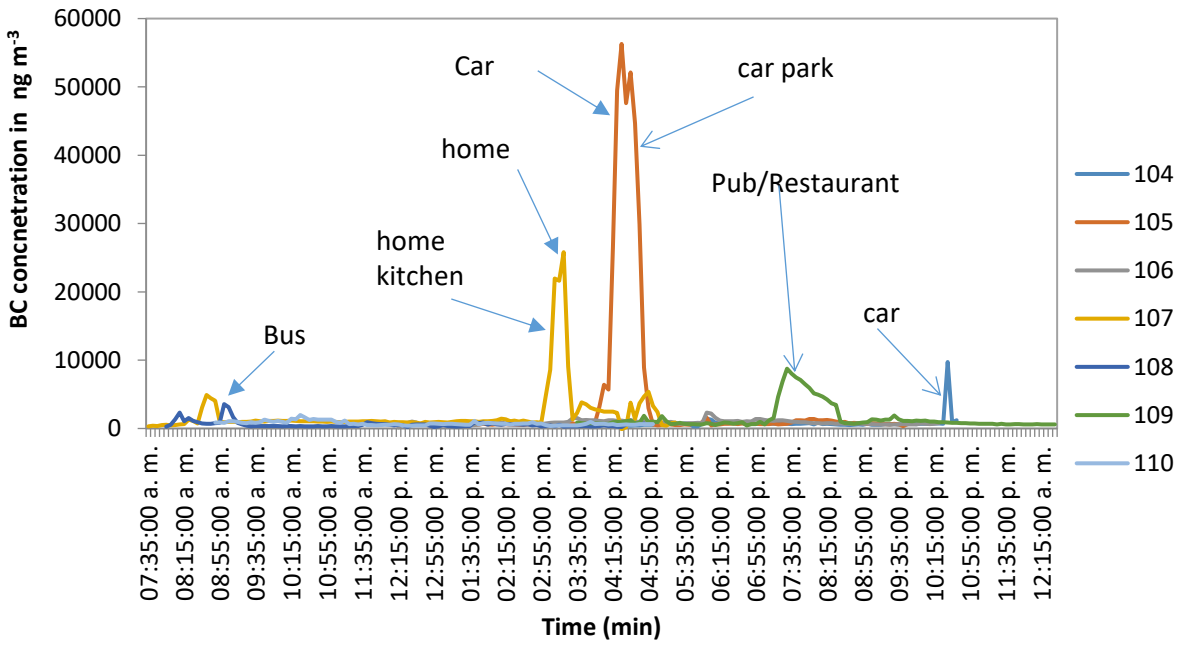


Figure III-7 Variability in the BC concentrations over the 24 hour period.

3.4.7 Wearability

To determine the comfort of the sampling bag and instruments, subjects were asked to fill in a questionnaire, which included questions on the type of bag for the sampling equipment. Subjects were also asked questions about their preferences on instruments and carrier bags, and their thoughts on having the instruments. The questions were structured in this order to finally have a broad overview of the sampling equipment. For instance, although several subjects preferred the sampling bag (6 of 10 subjects), at the end of the day, two of them expressed discomfort in carrying the backpack, and changed their response in the follow-up questionnaire to briefcase. Seven of the ten volunteers considered the briefcase too heavy.

Another issue tested in the questionnaires was noise produced by the equipment. Normally the pump by itself was not too noisy or the noise was reasonable and acceptable, but the sampling equipment set was composed of three pumps which together incremented the noise. On average, the noise was ranked 3.8 units, where 10 was very noisy and 0 was no laud. However, subjects expressed that the noise of the pumps was noticeable only during the night when no other noise was present. Therefore, most of the subjects decided to put the sampling equipment outside of the bedroom. With these considerations, the main objective was to design a backpack with insulating noise material, capable to keep the pumps ventilated.

Apart from the pumps, subjects were also asked to carry small instruments such as the VOC sensor, GPS, voice recorder and accelerometer. According to the results obtained from the questionnaire, most volunteers selected to carry the ASU sensor with a belt clip. On a scale of 1 to 10 where 10 was considered as fully satisfied, they considered that the belt was a good option (8.5 of satisfaction). A good rating (8.7) was also obtained for ease of carrying the instrument.

Six of nine subjects removed the device at one point in time, typically when they were sitting down or sleeping. The weight of the device was considered light (9 of 10) and the instrument was not deemed noisy. The subjects preferred the small GPS unit that can be added to the sampling bag, rather than the wrist-worn GPS unit. The use of the voice recorder was reported as a good tool for data collection. Volunteers were also requested to fill the draft FIXAT questionnaires for the purposes of testing and validation. The most

common comments included repetitive questions, difficulty in understanding some of the questions, and the lack of classification of questions.

In general, the wearability test was useful to advise the FIXAT subjects about the different options and the implication of having the chosen equipment set-up. In addition, it was a good tool to design the sampling bag and protocol needed to have a more accurate data and a more satisfactory sampling environment for volunteers.

3.5 Conclusion

Samples from eight volunteers were collected using the custom ASU sensor and the conventional integrate lab method. Results show good agreement between the cumulative concentration of the sensor with the lab results (R^2=0.83). However, the concentrations reported by the ASU sensor were higher than those obtained from the lab method. Negative intercept was observed due to the difference in the detection limit. Sensor and integrated samples are good tools to have TVOC concentrations, however although the use will depend on the objectives, both methods gave different information. The average formula is recommended to predict sensor concentration.

Having BC and VOC samples before starting the FIXAT project allowed us to gather preliminary information about possible sources that might influence the exposure concentrations. Based on the results from this pilot, high VOC concentrations were reported for commuter bus and BC for car users.

BC concentrations were found in specific locations such as car, pub and office, while VOCs covered a range of locations like car, pub, and office, train, bus, walking, parking car and outdoor environments.

With regard to wearability, most of volunteers chose the sampling backpack and considered it to be more comfortable. However, in cases where two backpacks needed to be carried, they suggested using one backpack and one briefcase. Discomfort about the noise was registered during the night-time. Although there were minimal observations in this section, both sampling bags were modified to isolate the noise. FIXAT possible questionnaires were tested and modified base on the volunteers' observation, which mainly were to clarify questions.

Based on the obtained results, it can be concluded that the physical characteristics of the instrument are reliable for the PE sampling as the instrument (ASU) is compact, and the instrument's app is user-friendly. However, further investigation should be conducted by using the sensor as the obtained concentration were higher compared with the integrated tube.

CHAPTER IV. RECENTLY REMODELLED OFFICES

4.1 Introduction

Since people spend around the 80 % of their time indoors (Harrison et al., 2009), high interest has been focused in determining the quality of these microenvironments. Several indoor sources and compounds have been identified. For instance, VOCs have been found in a range of microenvironments including homes, offices, restaurants/pubs, shopping centres, hair salons, schools and laboratories (Chan et al., 2002, Guo et al., 2004, Harrison et al., 2009, Jo and Kim, 2010, Delgado-Saborit et al., 2011a, de Gennaro et al., 2014, Neumann et al., 2014). Moreover, the VOC levels also depend on the products used or activities undertaken in the indoor microenvironments by the occupants (Yu and Crump, 1998, Stocco et al., 2008, D'Souza et al., 2009, Byun et al., 2010, Takigawa et al., 2012, Odabasi et al., 2014). VOC concentrations can be detrimental to the health and comfort of occupants in indoor microenvironments (Wolkoff, 1995, Yu and Jeong Tai Kim, 2010, Ongwandee et al., 2011, Takigawa et al., 2012, Weichenthal et al., 2012). Health effects associated with air pollution and particularly VOCs have been characterized in detail, and the International Agency for Research on Cancer (IARC) and the USEPA have classified benzene as carcinogenic (Malherbe and Mandin, 2007, Sarigiannis et al., 2011). VOCs have been reported to affect lung function and heart rate (Sarigiannis et al., 2011), neurological and respiratory [e.g. rhinitis, asthma] effects (Billionnet et al., 2011, Wu et al., 2012b), and chronic toxic risks (Sofuoglu et al., 2010). High cancer risk for benzene has been reported for new houses compared to old houses in many countries (Cohen et al., 2002, Zhou et al., 2011, Du et al., 2014) while exposure to other VOCs (e.g. styrene) in printer offices, classrooms and administrative offices has

been associated with high lifetime cancer risk (Cohen et al., 2002, Sliwinska-Kowalska et al., 2003, Guo et al., 2004, Destaillats et al., 2008, Tang et al., 2012). Exposure to VOCs in new houses can also increase the level of the Sick Building Syndrome (SBS) during the first and second year of the construction (Andersson et al., 1997, Takigawa et al., 2012).

Due to the possible contribution to VOC levels from products used in construction, remodelling or decoration of houses, researchers are increasingly focusing on studies to determine the effect of new or remodelled houses and the use of products such paint, wood preservatives, and glues; and the introduction of equipment, furniture, appliances and in offices and houses (Brown et al., 1990, Lee et al., 2003, Park and Ikeda, 2006, Armin et al., 2008, D'Souza et al., 2009, Yu and Jeong Tai Kim, 2010, Zhou et al., 2011, Maisey et al., 2013).

VOCs are believed to decay over time, and based on previous studies; reporting that compounds can take between 6 or 12 months to decay (Rothweiler et al., 1992, Yu and Crump, 1998, Järnström et al., 2006, Park and Ikeda, 2006, Bernstein et al., 2008, Hayashi and Osawa, 2013, Shin and Jo, 2013, Du et al., 2014). (Park and Ikeda, 2006) reported that VOC concentration in the new houses typically reach the level of the old houses by the third year. However, the rate of decay depends on several factors including the physical properties of the compound, ambient temperature (concentrations typically increase during spring and summer and decrease for the autumn and winter), ventilation or infiltration rate, and the product emission rate (which in turn is also influenced by the temperature). After that period of time, VOC concentration will depend only on the occupants' activities and used products (Wolkoff, 1998, Guo et al., 2009, Liang et al.,

2014). The number of compounds in new houses have been shown to be less than in the old houses in which more than 111 compounds were reported in Helsinki, Finland (Järnström et al., 2006).

4.2 Objective

The objective of this study was to measure the total VOC concentration in recently remodelled unoccupied offices and to assess the rate of decay of VOCs in new buildings.

4.3 Methodology

VOC samples were collected in newly remodelled offices in the School of Geography and Environmental Science at the University of Birmingham (UK). The two sampled offices were recently painted and remodelled, and new furniture was placed in the rooms. Continuous 24 hours samples (N=10) were collected in each office over a period of ten days in the summer of 2011. During the sampling collection, no other activity was performed in the offices as they were unoccupied. Samples were collected using sorbent tubes packed with a dual-adsorbent bed, which contained 300 mg of Tenax® GR (60/80 mesh) and 600 mg of Carbotrap™ (20/40 mesh), mounted on an ambient sampler with a flow rate of 40 cc min^{-1}. The contents of the tubes were extracted using thermal desorption and analysed using GC-MS following the methodology used in MATCH project and described in (Harrison et al., 2009). Statistical analysis was conducted using IBM SPSS V.20.

To test if the VOC decay is a first-order reaction, the natural logarithm of a reactant concentration versus time was plotted. Linear regression with negative slope, is

considered to be a first-order reaction, from which the first order decay coefficient (m^{-1}) can be obtained.

4.4 Results

4.4.1 New office concentrations

TVOC concentration is described as the sum of concentrations of all 20 compounds analysed in the study. The TVOC geometric mean for room one was 519 µg m^{-3}, and the concentration was almost two times higher than room two (310 µg m^{-3}). TVOC concentration observed in room one were similar or even higher than those reported in other studies which were conducted in new houses, while the concentrations seen in room two were lower than previous reported values in new houses (Järnström et al., 2006, Park and Ikeda, 2006, Armin et al., 2008, Shin and Jo, 2013, Du et al., 2014). In general, concentrations tend to decay over the sampling days (Järnström et al., 2006, Du et al., 2014, Rahman and Kim, 2014) (Figure IV-1). Variations were also registered in individual compounds throughout the sampling period (Table IV-1). Toluene was observed to be the most abundant VOC compound in the new offices. According to the literature toluene is one of the VOCs that is abundant in in new houses and this can be attributed to its presence in solvents, paints, and furniture and decoration materials. While benzene is often present in low concentrations since it is mostly found in cleaning products or deodorants (Park and Ikeda, 2006, Ongwandee et al., 2011, Guo et al., 2009, Liang et al., 2014, Rahman and Kim, 2014).

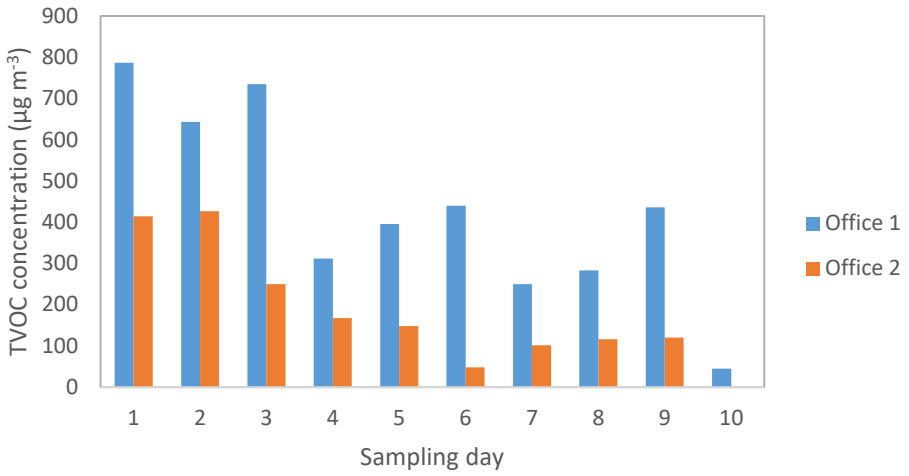


Figure IV-1 TVOC concentrations (sum of 20 VOCs) in µg m^{-3} by sampling day and comparing the two offices.

High molecular weight VOCs (e.g. xylenes), observed to be present in high concentrations in the offices sampled, are found in varnishing products, and their emission rates are highest during the first 10 hours after the application (Ongwandee et al., 2011). Several studies have reported high concentrations of xylenes together with the toluene and ethyl benzene (Lee et al., 2003, Maisey et al., 2013).

(Järnström et al., 2006) reported that while the concentration of xylene decreased with the occupancy, toluene registered the opposite trend, and there was an increase in its concentration with the occupant activities. BTEX compounds have been reported to be emitted from paints and glues and these compounds are influenced by temperature showing seasonal variations (D'Souza et al., 2009, Liang et al., 2014).

Initial concentrations of BTEX were higher in the current study compared to values reported for places like Japan [1.1 µg m^{-3} for benzene, 11.8 µg m^{-3} for toluene, 2.7 µg m^{-3}

for ethylbenzene and 5.8 µg m^{-3} for xylenes] (Takigawa et al., 2012) but lower than the results seen in new houses in China [benzene, toluene, m/p xylene and o-xylene were observed to be 18.5 µg m^{-3}, 173.2 µg m^{-3}, 58.1 µg m^{-3} and 40.8 µg m^{-3} respectively] (Du et al., 2014) .

Although dipentene concentrations fluctuated over the sampling period, high concentrations were registered occasionally. The primary indoor emission sources in indoor microenvironments are consumer products such as household cleaning products, plywood floor, sprays, fresheners products (Armin et al., 2008, Steinemann et al., 2011, Ongwandee et al., 2011, Moran et al., 2012, Maisey et al., 2013, Shin and Jo, 2013, Liang et al., 2014). Reported dipentene concentration for Japan ranged from 8.7 to 9.3 µg m^{-3}, where values were lower than those obtained in this study. Mean dipentene concentration of 35 µg m^{-3} in new Japanese houses was also observed (Park and Ikeda, 2006, Takigawa et al., 2012) whereas in Thailand, concentrations ranged from 113 to 241 µg m^{-3} levels that are higher than the obtained concentrations (Ongwandee et al., 2011). Floor or wall coverings can also emit compounds such as xylene, trimethylbenzene, benzene and styrene (Shin and Jo, 2013). Less volatile VOC compounds such benzaldehyde, octaldehyde and 2- ethyl-1-hexanol were found to be abundant in the new offices. The 2-ethyl-1-hexanol, part of the alcohol groups whose concentrations decrease rapidly, showed fluctuation in the concentration during the sampling period, consistent with previous studies (Liang et al., 2014). The group of aldehydes has also been reported to be high in new buildings, with benzaldehyde registered a concentration of 3.7 µg m^{-3} in Japan (Takigawa et al., 2012).

Table IV-1 VOC concentrations over a 10 days sampling period (μg m^{-3}) obtained from two recently remodelled offices.

Compound	Office 1										Office 2								
days	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8	9
Benzene	0.5	0.4	0.4	0.7	0.8	0.6	0.8	0.6	0.5	0.86	2.1	4.1	0.5	0.7	0.5	1.0	1.1	0.8	0.3
Toluene	167.3	178.4	344.6	36.7	54.1	62.9	27.5	26.3	37.0	33.1	71.2		28.4	17.9	16.9	4.7	15.7	8.4	8.2
Ethylbenzene	49.4	35.3	29.5	11.1	17.6	16.9	6.8	9.1	30.0	0.86	18.3	13.4	5.0	4.2	4.2	2.1	2.3	3.1	2.8
p-xylene	54.3	40.0	31.0	13.0	20.5	20.0	7.9	10.7	35.7	0.43	19.5	12.9	4.8	4.0	4.1	2.1	2.1	3.0	2.7
m-xylene	167.6	84.6	67.9	27.4	45.4	44.2	17.0	23.6	77.5	1.19	58.7	30.2	11.7	9.7	9.8	4.9	5.1	7.6	7.1
Pyridine	10.3	7.9	7.4	3.0	4.7	4.2	2.4	2.4	7.3	0.14	6.4	3.4	1.6	1.3	1.2	0.8	0.6	1.1	1.0
o-xylene	62.2	47.4	35.6	15.0	26.1	25.6	9.9	14.2	45.7	0.65	28.6	17.3	7.1	5.7	5.7	2.7	3.0	4.8	4.4
Cumene	1.6	2.0	1.8	0.6	0.8	1.4	0.6	1.0	1.1	0.05	2.2	1.9	0.8	0.4	0.4	0.1	0.3	0.4	0.3
Dipentene	16.4	33.4	33.3	18.1	26.7	48.1	24.2	37.1	27.8	0.83	14.9	76.1	15.8	10.0	12.7	2.2	6.9	9.7	8.7
n-propylbenzene	1.7	1.4	1.2	0.7	0.9	1.5	0.7	0.6	0.9	0.04	3.0	2.0	0.7	0.4	0.4	0.2	0.3	0.3	0.3
Styrene	1.7	2.1	3.5	2.5	3.2	3.8	2.5	3.2	3.5	1.25	1.0	9.5	0.9	0.7	0.7	0.3	1.2	0.7	0.7
p-isopropyltoluene	2.8	6.0	6.0	5.1	6.3	12.2	7.0	9.9	9.8	0.28	2.9	5.6	3.0	2.0	1.9	0.5	1.5	2.0	2.8
1,3,5-trimethylbenzene	1.4	1.3	1.4	0.9	1.1	3.0	1.3	1.1	1.6	0.03	3.1	1.0	0.6	0.4	0.4	0.2	0.3	0.3	0.4
1,2,4-trimethylbenzene	5.2	4.3	3.9	3.5	4.1	11.1	5.1	3.9	5.1	0.09	11.2	3.7	2.3	1.5	1.4	0.9	1.1	1.3	1.3
1,2,3-trimethylbenzene	2.5	1.8	1.3	1.8	2.0	6.5	2.8	1.9	2.2	0.04	8.3	1.9	1.2	0.7	0.7	0.3	0.5	0.6	0.6
Benzaldehyde	120.5	71.0	38.1	37.4	37.5	40.4	27.2	26.1	27.6	1.99		82.2	31.5	19.0	15.4	8.4	11.0	11.7	11.7
Octaldehyde	16.2	38.8	58.4	50.9	55.2	37.4	36.2	39.0	42.2	0.59	21.1	24.8	37.4	21.6	17.0	2.6	10.4	12.8	14.1
2-ethyl-1-hexanol	104.1	86.4	67.6	82.0	87.4	96.0	66.7	70.2	78.5	2.31	141.4	136.2	95.9	66.6	53.9	13.8	37.7	46.8	52.2
Naphthalene	1.2	1.0	2.6	1.3	1.4	3.7	2.9	2.1	2.1	0.07	0.6	0.6	0.6	0.5	0.5	0.3	0.4	0.5	0.5
TVOC	787	644	735	312	396	440	250	283	436	45	415	427	250	167	148	48	101	116	120

4.4.2 VOC decay rate

Results in section 4.4.1 show that over the ten day period, concentrations of the most office VOCs concentrations were found to decrease with time (Figure IV-1). It has been documented that these compounds decrease rapidly until the fourth month, and the decrease is subsequently slow until the first year. After two years it has been reported to reach old house concentrations (Park and Ikeda, 2006, Liang et al., 2014). To validate the exponential decrease, the first order decay was used.

By plotting the concentration versus the time, we can observe that some of the compounds such benzene, dipentene, styrene, p-isopropytoluene, octaldehyde, 2-ethyl-1-hexanol and naphthalene do not show exponential (Appendix 6) or linear trend (Appendix 7). No discernible VOC concentration trends have been reported during the first year of the decoration, or in most of the cases, measurements were not continuous. Furthermore, steady concentration had been reported after the third year (Järnström et al., 2006, Park and Ikeda, 2006, Hayashi and Osawa, 2013). In this study, the reaction rate coefficient was possible to be calculated as some of the compounds showed exponential decrement of the concentration. However, not all the exponential VOC decay profiles were first order reactions (ethylbenzene, p-xyene, pyridine, o-xylene). This was the case mostly for compounds in office one, in which concentration in day nine, might be influence by external factor or values on the ninth day might be an outliners. M-xylene and benzaldehyde in office, were the compounds that were possible to calculate the decay rate coefficient, and for both, values were a bit higher than the ones obtained in office two (Table IV-2). The decay rate coefficient for office two was calculated for all the compounds that showed exponential regression. On average, the decay coefficient was -0.24 day^{-1}.

The lowest decay rate coefficients was observed for pyridine an 1,3,5,-thrimethylbenzene (Appendix 7). The most abundant compounds and those that the decay rate coefficient was possible to be calculated (Toluene, ethybenzene, m-xylene, p-xylene, styrene and o-xylene) are known to be emitted from office products, decoration material and furniture (Ongwandee et al., 2011).

4.5 Conclusions

Recently redecorated offices were tested to determine VOC during the first 10 days of the redecoration. TVOC concentration of 20 analysed compounds show higher values for room one (519 µg m^{-3}) than room two (310 µg m^{-3}). Although previous results on new building VOC concentration had been reported, normally the result show difference between lapse time of months (eg. 3,6,12 month) or years (e.g. 1^{st},2^{nd} and 3^{rd} year). Moreover, most of the studies had sampled after one month of construction (Armin et al., 2008) omitting the first days. This is similar to what was done in the FIXAT study, where difference between the initial sample and final sample took after a year. Therefore because not consecutive measurements are taken, the decay rate is not possible to be computed. However, as previously mentioned, a steep decline in concentrations is observed during the firsts four months.

Based on results reported in the literature, there are significant variations in the emission rates of VOCs from construction products, and the rate of decay depends on the compound and source (Armin et al., 2008), therefore differences can be observed in year samples. Although high cancer risk and chronic respiratory problems are reported for new or recently renovated buildings (Du et al., 2014)

Table IV-2 VOC decay rate (d^{-1}) for two recently remodelled offices in Birmingham, UK.

Compound	Office 1			Office 2		
	Exponential R^2	First order R^2	Decay rate coefficient (d^{-1})	Exponential R^2	First order R^2	Decay rate coefficient (d^{-1})
Toluene	-	-	-	0.72	0.72	-0.24
Ethylbenzene	0.56	-	-	0.80	0.80	-0.22
p-xylene	0.50	-	-	0.80	0.80	-0.23
m-xylene	0.50	0.50	-0.31	0.75	0.75	-0.23
Pyridine	0.50	-	-	0.74	0.74	-0.21
o-xylene	0.43	-	-	0.73	0.74	-0.22
Cumene	-	-	-	0.70	0.71	-0.26
n-propylbenzene	-	-	-	0.70	0.76	-0.26
1,3,5-thrimetylbenzene	-	-	-	0.60	0.67	-0.21
1,2,4-thrimetylbenzene	-	-	-	0.63	0.70	-0.22
Benzaldehyde	0.63	0.63	-0.28	0.67	0.74	-0.24
1,2,3,-Trimetylbenzene	-	-	-	0.62	0.68	-0.26

It is important to estimate the acute effect from the exposure to VOC at new houses. Because the concentration was constantly decaying in room two, it was possible to calculate the decay rate coefficient for most compounds compared with room one. On average the decay coefficient was -0.24 d^{-1}. Further investigations might need to be conducted to consider several rooms either from offices, houses or other indoor microenvironments to determine if the decay rate is constant. Consider collecting paralleled temperature and humidity measurements and control as much as possible all the activities developed in the rooms.

CHAPTER V. PERSONAL AND INDOOR VOC EXPOSURE

5.1 Introduction

Urban air pollution has been on the increase primarily due to the anthropogenic activities, which primarily release pollutants such $PM_{2.5}$, PAHs, oxy-PAHs, VOC, and BC. These are mainly associated with traffic, industry or indoor activities causing adverse health effects on human health (Lan et al., 2013). However for epidemiological studies and assessment of health impact, it is necessary to have a more accurate measurement that reflects the real time- exposure of individuals. In fact, several authors have reported peak pollutant concentration during specific activities and speculated an increase in the associated risk of exposure (Huang et al., 2012a, Lim et al., 2012, McCreddin et al., 2013). However, high variability across individual activities, together with the outdoor sources, meteorological conditions, socio-demographic characteristics, ethnicity, age, gender and health conditions make it difficult to estimate average personal exposure, and futhermore the investigation results are largely representative for the sampled population only (Georgiadis et al., 2001, Jo and Kim, 2010, Lee et al., 2013). Reported results have shown differences between air pollutant concentrations at fixed monitoring stations and the personal exposure or indoor concentrations (e.g. home, office) (Michikawa et al., 2014). Moreover, it has been reported that people living in the same house can have different exposure levels and this is reflected in the differences in time activities (Lim et al., 2012, Buonanno et al., 2014). Providing specific location concentration of personal exposure and considering results from other places will be easier to create models to predict the personal exposure considering all the exposure determinants.

5.2 Objectives

To determine the effect on personal exposure and house concentration, caused by the construction or redecoration in the house.

To estimate the VOC difference between groups (two and three), sampling years (first and second sample) and sampling sites.

5.3 Methodology

5.3.1 Sampling methodology

For this study, adults from Birmingham, UK were recruited to participate as volunteers in a 24-h sampling campaign in order to characterize individual exposure to air pollutants such $PM_{2.5}$, PAHs, oxy-PAHs (CHAPTER VI), VOCs (CHAPTER V) and BC (CHAPTER VIII)**,** considering personal exposure, home and work sampling. The sampling methodology was the same for all the compounds. Subjects' selection and sampling criteria were obtained based on FIXAT objectives. In this section the focus will be on the VOC exposure.

5.3.1.1 Recruitment of volunteers

To conduct the personal exposure, home and workplace measurements, forty four healthy, non-smoking adult volunteer subjects were recruited. The selection criteria was based on different exposures to organic pollutants such as:

1) Subjects occupationally exposed to benzene;

2) Subjects living or working in new buildings (e.g. less than 1 year old) or buildings that had undergone redecoration in the previous year; and

3) Subjects not occupationally exposed and not living/working in new or renovated buildings (control group).

The recruitment method was through advertisements, pamphlets, e-mails, and friend request. The target groups were students and staff of the University of Birmingham. A Friendly request to friends and families was a key factor to recruit volunteers. For the work exposure (group one), the target groups were petrol station and garage workers and the owner/boss of the facility was contacted with information about the project and expectations from subjects. However, no favourable responses were received and it could have been due to the uncertainty around results from such a study. As a result, the recruitment strategy was altered and other kinds of occupationally-exposed subjects (e.g. gardeners, on-road workers) were approached.

For all groups, the recruitment method was divided in two stages, which was the initial and second contact. For the initial contact; the interested subject was given general information about the project and the work that was expected to be completed by them during the sampling time. If subjects were interested to participate, then in the second contact subjected were provided with a consent form, screening questionnaire and participant information sheet was given to them. All requisite ethics approvals were sought before commencing the recruitment. Finally, using the screening questionnaire (Appendix 8) the subjects were selected and enrolled in the project.

Based on the screening questionnaires, plausible subjects for group one, subjects occupationally exposed, were excluded if they lived in a new or recently remodelled

house. In group two, subjects were chosen based on whether they lived in a new or recently redecorated house or office, and any subjects with exposure to VOCs at work were excluded. Selection did not take into specific account age, gender or ethnic background, and the travelling time from home to work was not used as an exclusion criteria. Finally, subject were request not to change the normal activities during the sampling day.

5.3.1.2 Sampling campaign

A total of 14 volunteers were recruited in group one, 15 in group two and 15 in group three. For groups two and three, 24 hour sampling period was taken from all the volunteers. For group one, the sampling period was 8 hours, corresponding to the normal working hours. Volunteers in group two were also requested to undertake a second sampling which took place a year from the first sampling (Table V-1). The main objective was to have the sampling measurements to see if there was any difference in pollutant concentrations a year after the construction or re-decoration of the house or office (longitudinal study).

Table V-1 Subjects recruitments and sampling criteria

Group	Number of volunteers	Sampling type	Sample duration (hours)	Repeated samples
1	14	Work	8	No
2	15	New houses	24	After a year
3	15	Control	24	No

The volunteers were requested to carry a backpack/briefcase to measure personal exposure. Additional briefcases were placed in their homes for 24-hours and in some

cases, at work for 8-hours. For subjects in group one, only personal exposure samples were collected and no additional sampling equipment was handed out for home or work microenvironments.

The backpack/briefcase contained a suite of instruments for sampling different air pollutants- an SKC pump connected to a sorbent tube for VOCs, Casella pump connected with a $PM_{2.5}$ cyclone and Teflon filter for $PM_{2.5}$, PAHs and oxy-PAHs, a microAethalometer (AE51) for real time BC concentrations and a $PM_{2.5}$ real-time sensor MicroPEM. The last two instruments were only placed in the personal exposure sampling bag.

Subjects from group two and three were sampled in warm and cold seasons, while for group one, samples were collected between March and May (Table V-2). A second sample from subjects in group two; although , in some cases the samples collected may not have been exactly collected in a year all of them were collected during the same month as the first year sample.

Table V-2 Sampling location and period

Group	Sampling locations	Sampling period
1	Work	March –May
2	Work, home and PE	March –June September – November
3	Work, home and PE	March –June September – November

Volunteers' sample collection was in series as only one sampling bag with all the instruments was available, and during the week days. This is to take in consideration the

low variations in activities on weekday (when volunteers work, stay at home etc.) compared with weekends.

5.3.2 Subject related information

To characterize the personal exposure and the microenvironment, subjects were asked to complete a Time Activity Diary (TAD) and complementary questionnaires (Appendix 3). These provided useful information about the places, journeys and activities done during the sampling day, as well as the characteristics of the house that might influence the concentration of the pollutants. To optimize the time, volunteers were provided with a voice recorder to record all the activities conducted during the sampling day.

5.3.2.1 Sampling equipment

5.3.2.2 Sampling bag optimization

To achieve the main objectives, it was necessary to develop sampling equipment with specific characteristics, such as low weight, low-noise and 24-hours throughput, according to the recommendation proposed during the ASU-FIXAT pilot project. The objective was to take samples of all the compounds at the same time, without having too much weight or noise and providing greater comfort for carrying the sampling bag. To reduce the noise, the briefcase and the backpack were tested using different noise insulating material. Volunteers were asked about the noise and comfort by carrying; either a briefcase or a bag- pack and filling the usability test questionnaire (Appendix 4). The HITACHI VM-NP500H Camcorder Battery Replacement (Li-ion, 7.2 V, 1850 mAh, 0.23 kg) batteries were found to be the most suitable among the available options, and were used for all sampling events.

5.3.2.3 Sampling instruments

The VOCs were sampled using stainless-steel sorbent tubes (length -17.8 cm, external diameter- 0.6 cm) connected with a SKC (PCXR8) pump, running with a flow rate of 40 mL min^{-1} for 24 hours. The tubes were packed with a dual-adsorbent bed, which contained 300 mg of Tenax® GR (60/80 mesh) and 600 mg of Carbotrap™ (20/40 mesh). The packed sorbent material was purchased from Supelco (Dorset, United Kingdom). Unsilanised glass wool was used to separate the tube from the sorbent material. Finally the tubes were sealed using ferrules and swagelok caps, 316 SS VCR Face Seal Fitting, 1/4 in (Delgado-Saborit et al., 2009).

The tubes were conditioned at 275˚C for one hour in the GC oven connected to the N_2 cylinder, the nitrogen flow was between 80 to 120 cc min^{-1}. The oven parameters for conditioning were set according to the SOP given in MATCH project (Harrison et al., 2009) and described in Table V-3. After conditioning, the tubes were wrapped in aluminum foil and stored in the refrigerator at 4 ˚C, before and after sampling.

Table V-3 GC oven parameters for conditioning of the sorbent tubes.

PARAMETER	CONDITIONS
Initial temperature	33°C
Initial time	10 min
Rate	8°C min^{-1}
Final temperature	275°C
Final time	60 in

5.3.3 VOC analysis

Prior to analysis of the samples in the GC-MS, internal standards (Table V-4) were injected into the tubes and nitrogen was flushed through at 20 mL min^{-1} for 10 min to

ensure standard dispersion through the tube and to make certain that the solvents had evaporated.

Table V-4 VOC internal standards.

Compound	Concentration ng μL^{-1}	Final mass ng
Ethylbenzene D10	23.6	236
Toluene D8	25	250
Naphthalene D8	25	250
Styrene D8	23.7	237
Benzene D6	23.6	236

The samples were mounted on the Aero trap auto-sampler Thermal Desorption instrument (TD). The sample was heated for a period of time and retained in the TD unit to be release and transferred to the cooled cryotrap (Tekmark 6000 model) by using helium as a carrier gas. Finally, after finishing the desorption process the sample was transferred from the cryotap to the GC to be separated and analyzed in the MS. The method used for desorption and analysis was the same used by the MATCH project (Harrison et al., 2009). The desorption conditions parameters are listed in Table V-5.

Agilent Technology system (6890 N) GC fitted with a wax 52C13 capillary column was used, which uses helium as a carrier gas to inject the sample into the GC column where the compounds are separated and then transferred to the detector (Agilent 5973 N) where the compounds are identified. Table V-6 shows the GC-MS system conditions.

Table V-5 Thermal desorption conditions.

PARAMETERS	CONDITIONS
Line temp	200
Valve temp	200
MCS line temp	50
Trap standby	200
60xx valve	200
60xx line	200
Trap cooldown	-30
SMPLsweep	PRE-cool
Sample SWP time	0.00 min
Sample des time	20.00 min
Sample des tem	250
Cryofocuser	Off
Des preheat	250
Trap desorption time	4.00 min
Trap desorption tem	250
Sample bake	275
Bake time	10.00 min
Trap bake tem	275
MCS bake tem	300

.**Table V-6 GC-MS conditions to analyse VOC.**

	PARAMETERS	CONDITIONS
CG	Injector temp	250
	Initial temperature	40˚C
	Maximum temp	325˚C
	Initial time	5.00 min
	Equilibration time	0.50 min
	Post temp	5˚C
	Post time	1.00 min
	Run time	25.00 min
MS	Carrier gas	Helium
	Mode	Split (100:1)

The masses monitored for each target VOCs alongside with the qualifier and retention time are summarized in Table V-7. The chromatograms were checked using the MSD Chem-station software and data was transferred to an Excel file for the statistical analysis

Table V-7 Target natural VOC compounds.

COMPOUND	RETENTION TIME (MIN)	TARGET ION ($M^{+)}$	QUALIFIER ION (M+)
Benzene	7.01	78	77
Toluene	9.68	91	92
Ethylbenzene	12.38	91	106
p-xylene	12.64	91	106
m-xylene	12.85	91	106
Cumene	13.90	105	120
pyridine	14.25	79	52
o-xylene	14.26	91	106
Dipentene	14.67	68	93
n-propylbenzene	15.03	91	120
1,3,5- Trimethylbenze	16.14	105	120
Styrene	16.57	104	78
p-isopropyltoluene	16.94	119	134
1,2,4-Trimethylbenze	17.28	105	120
Octylaldehyde	17.52	43	56
1,2,3-Trimethylbenze	18.92	105	120
2-ethyl -1-hexanol	23.04	57	83
Benzaldehyde	24.09	77	105
3-vinylpyridine	27.22	105	104
Naphthalene	29.31	128	93

5.3.4 Statistical analysis

The data were analysed using Excel (version 2013), SPSS (version 22) and Access (version 2013). Concentrations were tested for normality by using skewness statistic, and in case of showing not normality, data was (ln) transformed for the statistical comparisons. To identified statistical differences between two levels, a t-test was used and ANOVA for

more than two levels. When statistical differences were observed using the ANOVA a test for mean comparison was used (Tukey, $p< 0.05$). In the case of comparing groups with different N, a type III error in the ANOVA was applied. The comparisons were made compound-by-compound and in other cases considering the different stratus.

5.4 Results

5.4.1 General study population

Table V-8 shows information of the sampling recruitment characteristics for the FIXAT project. Occupationally exposed subjects were monitored only for VOC during working hours.

Table V-8 Volunteer recruitment characteristics.

Group	No. of volunteers	Sampling Characteristics	Sample duration (hours)	Repeated samples	Analysis
1	14	Occupational exposed	8	No	VOCs
2	15	new houses	24	After 1 year	BC, $PM_{2.5}$, PAHs, oxy-PAHs and VOCs
3	15	Control	24	No	BC, $PM_{2.5}$, PAHs, oxy-PAHs and VOCs

Since air pollutant concentrations may differ based on the different activities that subjects perform, several factors including gender, age or ethnicity were considered in characterizing personal exposure. The gender distribution was almost 1:1 with 57 % male and 43 % female participants. Most of the volunteers were in an age range between 18 and 35 years, and six volunteers were older than 35 years. While the largest number of

subjects were Europeans; other countries including Mexicans, Indians and South Koreans were also recruited.

Table V-9 House characteristic per sampling group (%).

	Group 1 (N=14)	Group 2 (N=15)	Group 3 (N=15)
	House characteristics		
Semi-detached	70	86	93
Sub urban	92	80	87
Have garage	50	13	13
	Type of heating		
Natural gas	76	64	50
Electricity	15	21	37
	Cooking fuel		
Natural gas	84	57	25
Electricity	15	42	75
	Work Category		
Office worker		20	20
Gardening	36		
Housewife		6.7	6.7
Student		60	73.3
Unemployed		13.3	
Roadwork	64		
	Occupation description		
Open air work	100		
Office work		20	6.7
Indoor work, but not office		60	86.7
Printers in the office		6.7	6.7
Handle solvents	68		
Use tools (which contain fuel or solvent	53		

Although house location and characteristics were not considered as selection criteria, most volunteers resided in terraced and flat houses mostly in the urban and sub urban area. Those who reported to have an attached garage to the house were the volunteers

recruited for group one, however for those subjects, home and office concentration were not monitored. Natural gas and electricity were the main fuel used to heat and cook, except for group three which main fuel for cooking was the electricity (Table V-9).

Because most of the time is spent in indoor microenvironments, volunteers were asked to describe the work place as a main factor that may contribute to the personal exposure concentration. Group one was composed of road workers with 64 % and gardeners with 36 %. Both categories reported to work in open air environments. From the total of subjects in group one, 68 % reported handling solvents and 53 % used tools that required oil or fuel. All subjects reported working in open air most of the time. The predominant occupation across the volunteers in groups two and three was students and office workers. Students reported to work in indoor microenvironments but not necessarily as an office (Table V-9). Although, the sampling population will not represent all the Birmingham population, the sampling group will contribute to understanding the pollutant behaviour, considering the specific sampling characteristics and avail previously published data related to the same topic even though the ambient conditions were different.

The TAD was used to record the activities developed during the day, the times and locations were corroborated with the voice recorder. Although in the questionnaire a guide of the time was given with intervals of 30 min, volunteers were asked to write the exact time of shift activities (Appendix 3). Other parameters in the TAD included activity type, location, open/closed windows, smoking (self, or second-hand exposure) and level of exercise.

Volunteers' activities were categorized into five main microenvironments including outdoor, in-transit, home, work and other indoor activities (Figure V-1). In this study, participants were found to spend around 64 % of the time at home, 23 % at work, 8 % in transit and 1 % outdoors. This is similar to the estimated 60 to 80 % time spent indoors in previous studies (Buonanno et al., 2014, Choi and Spengler, 2014, Gu et al., 2014, Gariazzo et al., 2015). It is important to note that differences in the time spent in various microenvironments can vary due to differences in lifestyles such as sedentary vs active or workaholic with passive workers.

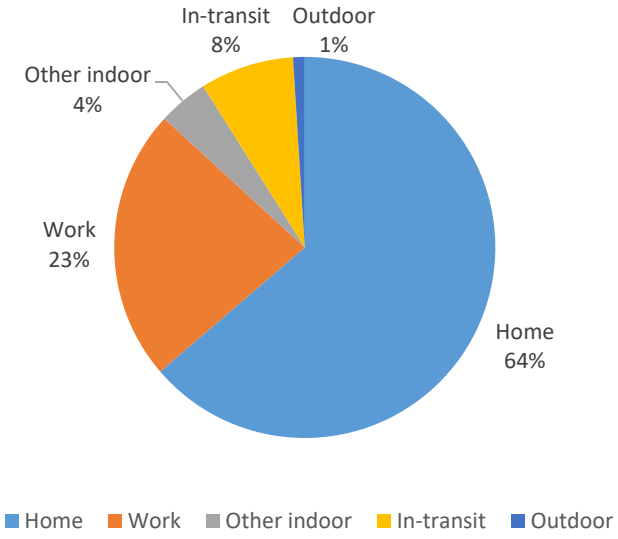


Figure V-1 Average time spent in different microenvironments across volunteers.

5.4.2 VOC study population

Subjects selected to participate in this projects were recruited based on the VOC exposure. The measured environments were home, work and personal exposure for group two and three, while for group one only work exposure samples were obtained as subjects were not willing to participate. Home sampling was conducted during the first

months up to 12 month of the decoration, therefore subjects in group two subjects were sampled after a year of the construction or decoration (Table V-10). The analysed correlations were:

a) Year 1 from group two and three,

b) Group two difference between year 1 and 2 and

c) Work for all the groups during the first year and new office vs FIXAT new houses.

Table V-10 sampling group to determine VOC concentrations.

	Group 1		Group 2		Group 3	
year	**1**	**2**	**1**	**2**	**1**	**2**
Personal (PE)	NM	NM	15	12	16	NM
Home (H)	NM	NM	14	11	16	NM
Work (W)	12	NM	8	4	10	NM

NM- Not measured 1- year 1, 2- second sample after a year.

5.4.3 VOC by groups (2 and 3) during the first year (new/old house)

In order to determine the difference between recently remodelled houses and old houses, home microenvironment concentrations for first year samples from group two (redecoration/remodelling) were compared to concentrations observed in group three (no redecoration/remodelling) (Table V-10). Independent t- test was used to estimate the difference between groups (p=0.05). The analysis was done separately for personal exposure (PE), Home (H) and Work (W) considering compound-by compound.

PE differences were observed for compounds such toluene, dipentene, n-propylbenzene, styrene and benzaldehyde; reporting higher concentration from group two (new or recently

redecorated houses) Previous studies conducted on new or recently redecorated houses have reported high abundance of compounds such toluene, styrene and dipentene (Park and Ikeda, 2006, Guo et al., 2009, Su et al., 2013, Du et al., 2014). However, no statistical difference was observed from home samples, except styrene, indicating that PE concentrations were influenced from other emission sources more than from construction or decoration material. Although the styrene concentrations (2.19 µg m^{-3}) were relatively high for new houses in the current study, higher values have been reported for new houses for example; Hong Kong with 10.9 µg m^{-3} (Guo et al., 2009) and Japan with 64 µg m^{-3} (Park and Ikeda, 2006). Concentrations of toluene (27/15 µg m^{-3}) and dipentene (35/31 µg m^{-3}) in Japanese new/old houses were higher than the values observed in the FIXAT study (19/14.52 µg m^{-3}) (Park and Ikeda, 2006). In Athens, toluene concentration was found to be higher than the current study (50/15 µg m^{-3}) (Baya et al., 2004).

In general, PE concentrations were higher than home. Although PE concentrations are mainly influenced by the indoor activities a large contribution to the exposure has been reported to be from the outdoor sources, therefore, results suggest that the higher exposure was recorder while subject commute. (Kim et al., 2001, Su et al., 2013), Primary PE identified sources had been reported to be traffic emissions and cleaning products (Edwards et al., 2001, Lau and Chan, 2003, Wang et al., 2009). Higher exposure can be observed while subjects commute by car and bus, and a large amount of TEX was observed for those transports using air conditioners (Lau and Chan, 2003, McNabola et al., 2008).

Table V-11 VOC concentrations considering the sampling group and the sampling type (µg m^{-3}).

	Group 2						Group 3					
	PE (N=15)		Home (N=14)		Work (N=8)		PE (N=15)		Home (N=16)		Work (N=10)	
Compound	GM	GSD	GM	GSD	GM	GSD	GM	GSD	GM	GDS	GM	GSD
Benzene	1.56	2.01	1.54	2.37	2.07	1.56	1.61	2.95	2.14	2.29	1.56	1.82
Toluene	40.16b	3.47	19a	4.72	59.26b	5.63	9.99a	4.13	14.52a	4.36	12.39a	4.23
Ethylbenzene	1.19	2.60	1.22	1.93	1.67	1.96	1.05	1.92	1.55	2.48	1.28	2.87
P-Xylene	0.79	2.91	0.77	1.90	1.25	2.01	0.78	1.71	1.03	2.32	0.8	2.54
M-Xylene	1.98	3.00	2.05	1.98	3.39	2.05	2.08	1.84	2.75	2.33	2.31	2.61
Pyridine	0.51	2.87	0.34	7.27	0.77	2.56	0.23	6.53	0.24	8.51	0.85	5.91
O-Xylene	1.19	3.24	1.24	2.00	2.1	2.12	1.28	1.88	1.56	2.27	1.43	2.88
Cumene	0.15	2.79	0.15	2.43	0.14	2.48	0.21	8.51	0.3	8.65	0.06	2.85
Dipentene	36.73b	4.88	34.70a	2.75	70.30b	3.67	14.1a	21.34	29.21a	4.98	30.38a	8.56
N-Propylbenzene	0.30b	2.96	0.29a	3.04	0.25a	2.06	0.17a	2.07	0.26a	4.43	0.15a	2.68
Styrene	2.19b	2.97	1.90b	3.57	1.22b	2.29	0.69a	2.61	0.81a	2.30	0.79a	3.16
P-Isopropyltoluene	2.42	4.17	3.48	2.36	1.98	4.31	1.63	3.16	2.32	3.15	0.84	5.26
1,3,5 Trimethylbenzene	0.36	4.47	0.54	3.38	0.37b	1.91	0.26	5.81	0.54	2.78	0.15a	2.88
1,2,4 Trimethylbenzene	1.2	4.49	1.85	3.55	1.24b	1.95	0.88	1.95	1.46	2.66	0.47a	2.67
1,2,3 Trimethylbenzene	0.52	4.85	0.75	3.73	0.52b	2.48	0.55	3.66	0.86	4.48	0.18a	2.72
Benzaldehyde	4.13b	1.70	3.6	1.81	5.56a	1.92	2.33a	3.26	2.98	2.34	3.74a	1.98
Octaldehyde	5.41	2.09	6.13	2.23	4.45	2.46	5.82	1.70	7.93	1.84	4.86	2.67
2 Ethyl 1 Hexanol	19.36	3.31	22.45	4.00	26.83	2.42	8.44	12.48	10.87	5.73	17.02	2.94
Naphthalene	1.85	6.63	1.31	8.29	1.44	3.13	1.4	3.52	1.78	7.38	0.62	2.90

A t-test ($p < 0.05$) has been used to test for statistically different concentrations between Group 2 and Group 3 (e.g. PE Group 2 versus PE Group 3). Numbers shown in bold were statistically different as indicated by the different letters associated with each. For the concentrations in normal font, there was no significant difference.

5.4.4 Group two comparison between the first and second sample

Group two was sampled twice (with an interval of 12 months) at the personal, home and work microenvironments. Home samples, in which the main objective was to look for the decay of the compound at new or recently redecorated house and after a year were analysed (Table V-12). The main difference between the years is that dipentene was in higher concentration in the first year, when the houses were recently redecorated or constructed (Independent t-test, $p>0.05$). However, the effect of indoor sources can be observed in the high concentration reported for p- and o- xylene and cumene during the second year which might vary depending of the indoor activities. Moreover, for work microenvironment, concentration of dipentene was similar for both samples which could indicate a specific work source. BTX sources include, decoration material, new furniture, solvents, paints and adhesives (Ongwandee et al., 2011, Du et al., 2014). Dipentene is reported to be present in paints and cleaning products because of its characteristic lemon-like odour (WHO, 1998). It is also emitted from plywood flooring, sheet vinyl flooring, refreshing sprays, and windows spray cleaner (Armin et al., 2008, Ongwandee et al., 2011).

According to the literature, VOC registered the higher decrease of concentrations during the first 6 months up to 12 months (Järnström et al., 2006, Park and Ikeda, 2006, Armin et al., 2008, Hayashi and Osawa, 2013, Shin and Jo, 2013). Dipentene concentration in the FIXAT study was found to decrease from 34.70 to 4.72 µg m^{-3} in the home microenvironment, while in case of PE, concentrations decreased from 36.73 to 3.53 µg m^{-3}. Lower dipentene concentrations were report for new or recently remodelled houses

in Hong Kong 18.1 µg m^{-3} (Guo et al., 2009), however, (Ongwandee et al., 2011) reported a concentration of 60.5 µg m^{-3} in Thailand. Contrary to these results, in Finland, (Järnström et al., 2006) found no differences across three samples taken in a 12 moths period, reporting values of 12, 10 and 12 µg m^{-3}. Similar results were reported by (Park and Ikeda, 2006) in Japan, where concentrations for three consecutive years were 35, 29 and 32 µg m^{-3} where no statistical different was found similar what occurs with the work concentration in which not statistical difference was observed between years. In China, (Liang et al., 2014) reported an increment at the end of the 12 month period from 24.2 to 39.1 µg m^{-3}, arguing that by that time the concentration are more influenced by the human activities.

Table V-12 VOC concentrations obtained for the initial and second sample from group 2 (µg m^{-3}).

	Initial sample from group 2						Second sample (after a year) from group 2					
	PE (N=15)		Home (N=14)		Work (N=8)		PE (N=12)		Home (N=11)		Work (N=4	
	GM	GSD	GM	GSD	GM	GSD	GM	GSD	GM	GSD	GM	GSD
Benzene	1.56	2.01	1.54	2.37	2.07	1.56	2.44	1.69	2.56	1.65	1.99	1.97
Toluene	**40.16b**	3.47	**18.99a**	4.72	**59.26b**	5.63	**11.23a**	1.34	**16.50a**	1.52	**14.41a**	3.99
Ethylbenzene	1.19	2.60	1.22	1.93	1.67	1.96	1.74	1.58	2.00	1.57	2.02	1.45
P-Xylene	**0.79a**	2.91	**0.77a**	1.90	**1.25a**	2.01	**1.49b**	1.60	**1.75b**	1.59	**1.78a**	1.45
M-Xylene	1.98	3.00	2.05	1.98	3.39	2.05	3.77	1.60	1.98	3.09	4.64	1.34
Pyridine	0.51	2.87	0.34	7.27	0.77	2.56	0.10	4.06	0.10	4.48	1.03	2.02
O-Xylene	**1.19a**	3.24	**1.24a**	2.00	**2.10a**	2.12	**2.11b**	1.63	**3.37b**	1.82	**3.02a**	1.32
Cumene	**0.15a**	2.79	**0.15a**	2.43	**0.14a**	2.48	**0.95b**	3.76	**1.04b**	3.01	**0.13a**	1.22
Dipentene	**36.73b**	4.88	**34.70b**	2.75	**70.30b**	3.67	**3.53a**	4.72	**4.72a**	5.34	**52.48a**	2.31
N-Propylbenzene	0.30	2.96	0.29	3.04	0.25	2.06	0.31	1.59	0.45	1.73	0.22	1.12
Styrene	2.19	2.97	1.90	3.57	1.22	2.29	0.94	1.53	1.31	1.56	1.16	2.11
P-Isopropyltoluene	2.42	4.17	3.48	2.36	1.98	4.31	1.27	1.89	2.53	1.87	2.00	1.89
1,3,5 Trimethylbenzene	0.36	4.47	0.54	3.38	0.37	1.91	0.93	1.88	1.39	1.85	0.37	1.27
1,2,4 Trimethylbenzene	1.20	4.49	1.85	3.55	1.24	1.95	1.53	1.70	2.79	1.88	1.33	1.26
1,2,3 Trimethylbenzene	0.52	4.85	0.75	3.73	0.52	2.48	1.52	2.21	1.80	2.01	0.56	1.64
Benzaldehyde	4.13	1.70	3.60	1.81	5.56	1.92	1.41	1.71	1.12	2.36	4.53	1.48
Octaldehyde	5.41	2.09	6.13	2.23	4.45	2.46	4.17	1.58	4.01	2.75	6.66	4.02
2 Ethyl 1 Hexanol	19.36	3.31	22.45	4.00	26.83	2.42	1.30	5.18	3.19	4.29	20.10	2.57
Naphthalene	1.85	6.63	1.31	8.29	1.44	3.13	1.15	1.81	0.57	3.22	1.42	4.90

A t-test ($p < 0.05$) has been used to test for statistically different concentrations between sampling year (e.g. PE year 1 versus PE year 2). Numbers shown in bold were statistically different as indicated by the different letters associated with each. For the concentrations in normal font, there was no significant difference.

And in an interval period of 1,6,12 and 24 months, (Shin and Jo, 2013) reported dipentene concentrations of 19, 14, 9.7 and 8.5 µg m^{-3} respectively in Korea. In general, dipentene concentrations were a good indicator of the construction material as the difference between years.

Toluene was reported to be one of the most abundant compounds in new or recently remodelled houses (Du et al., 2014, Liang et al., 2014, Park and Ikeda, 2006, Ongwandee et al., 2011). Toluene concentration in the FIXAT samples decreased after a year in PE from 40.16 to 11.23 µg m^{-3} and work from 59.26 to 14.41 µg m^{-3}. However, home concentrations did not show statistically significant differences. It is important to note that toluene is a very volatile compound, and can be only observed in acute measures as in cases observed for PE and work. The initial values obtained for FIXAT samples were lower than those reported for Guangzhou, China [173.2 µg m^{-3}] (Du et al., 2014), Beijing, China [46 µg m^{-3}] (Liang et al., 2014) and Thailand [110 µg m^{-3}] (Ongwandee et al., 2011). Previous studies have also reported a decrease in toluene concentrations between years. (Shin and Jo, 2013) reported a decrease from 103 to 35 µg m^{-3} over a 24 month period in Korea. (Park and Ikeda, 2006) reported a decline in VOC concentrations over a 48 month period (27 to 11 µg m^{-3}).

5.4.5 Work exposure difference between groups (1-3)

Work samples were obtained from three groups, occupationally exposed to VOC (1), new or recently decorated house, however office were not new (2) and control group (3). Therefore we can say that, group two and three were almost similar work environments (office).

During the FIXAT sampling campaign, group one comprised of subjects that might be exposed to VOCs at the work place, and the main activities of the volunteers included gardening and road work. To determine the influence of work-related activities on personal exposure, work-related exposure for volunteers from the three sampling groups were compared.

Results showed a statistical difference between group two and three with group one for most of the compounds (One way ANOVA, p=0.05), displaying the highest concentrations for group one (subjects exposed to VOC at their work microenvironments), except for pyridine, dipentene, p-isopropyltolunene and 1,3,5 trimetylbenzene, benzaldehyde, octaldehyde 2-ethyl-1-hexanol and 3- vinylpiridine, for which higher values were observed in groups 2 and 3 (Table V-13).

Outdoor workers are normally exposed to traffic emissions and VOCs as one of the predominant compound groups (Fischer et al., 2000, Chan et al., 2002, Tovalin-Ahumada and Whitehead, 2007, Massolo et al., 2010). In this study, BTEX and cumene were the most abundant compounds although heavier VOCs were also found in high concentration for outdoor workers. Obtained concentration were similar to the reported for Hong Kong, China (Chan et al., 2002) in compounds such benzene, toluene and cumene. However, for ethylbenzene, xylenes and styrene higher concentrations were obtained for this study.

Table V-13 VOC concentration by sampling group at the work environment (µg m^{-3}).

Compound	Group 1 (N=12)		Group 2 (N=8)		Group 3 (N=10)	
	GM	GSD	GM	GSD	GM	GSD
Benzene	24.39b	3.18	2.07a	1.21	1.56a	1.30
Toluene	65.29b	1.36	59.26b	2.12	12.39a	1.87
Ethylbenzene	18.99b	1.57	1.67a	1.34	1.28a	1.58
P-Xylene	21.99b	1.65	1.25a	1.35	0.80a	1.50
M-Xylene	39.86b	1.51	3.39a	1.37	2.31a	1.52
Pyridine	1.80a	1.67	0.77a	1.50	0.85a	2.16
O-Xylene	26.11b	1.57	2.10a	1.39	1.43a	1.58
Cumene	71.21b	2.21	0.14a	1.48	0.06a	1.58
Dipentene	0.03a	1.33	70.30b	1.76	30.38b	2.54
N-Propylbenzene	5.44b	1.61	0.25a	1.37	0.15a	1.53
Styrene	9.31b	1.61	1.22a	1.43	0.79a	1.65
P-Isopropyltoluene	2.47a	1.60	1.98a	1.89	0.84a	2.06
1,3,5 Trimethylbenzene	0.45a	2.50	0.37a	1.32	0.15a	1.58
1,2,4 Trimethylbenzene	21.81b	1.49	1.24a	1.34	0.47a	1.53
1,2,3 Trimethylbenzene	28.03b	1.29	0.52c	1.48	0.18a	1.54
Benzaldehyde	5.72a	1.58	5.56a	1.33	3.74a	1.35
Octaldehyde	7.65a	1.53	4.45a	1.48	4.86a	1.53
2 Ethyl 1 Hexanol	0.04a	1.68	26.83b	1.47	17.02b	1.60
Naphthalene	5.51b	1.25	1.44a	1.64	0.62a	1.59

ANOVA ($p < 0.05$) has been used to test for statistically different concentrations between Groups. Numbers statistically different are indicated by the different letters associated with each.

On the other hand, obtained values were higher than the observed in La Plata, Buenos Aires (Massolo et al., 2010) and for Rome, Italy (Ciarrocca et al., 2012), and lower than those reported for Mexico city (Tovalin-Ahumada and Whitehead, 2007) and Bangkok, Thailand (Tunsaringkarn et al., 2014). Exposure to BTEX has been associated with an increase in respiratory problems and reduction of the spirometric index for outdoor workers (Choudhary and Tarlo, 2014) and benzene associated with a higher cancer risk (Tunsaringkarn et al., 2014).

In contrast, concentrations of dipentene and toluene were found to be higher for indoor workplaces. In indoor environments, these compounds are normally associated with fresheners, cleaning products, deodorants and spray products (Ongwandee et al., 2011, Rahman and Kim, 2014) or emissions from printers and photocopiers (Lee et al., 2001, Destaillats et al., 2008, Sarkhosh et al., 2012). In Thailand, Ongwandee et al. (2011) found toluene (110 µg m^{-3}) and dipentene (60.5 µg m^{-3}) to be the most abundant VOCs in offices (Ongwandee et al., 2011) (Table V-14).

5.4.6 Office and FIXAT comparison

New and recently remodelled offices concentrations were considerably higher than those obtained for group two in the first year in the FIXAT cohort (new and recently remodelled houses) for compounds with low molecular weight like toluene, ethylbenzene, xylenes, pyridine and n-propylbenzene (Table V-15). However, compounds with low volatility such as 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, benzaldehyde, octaldehyde and 2-ethyl-1-hexanol exhibit higher concentrations for new offices than for new houses. Based on this information, we can say that some possible reasons can be firstly; that office samples were collected just after the

remodelling was completed, while samples from new homes in the FIXAT project were collected within three months after the remodelling.

Table V-14 Summary of VOC concentrations reported for outdoor workers and traffic relate concentrations (µg m^{-3})

References	(Chan et al., 2002)	(Massolo et al., 2010)	(Tovalin-Ahumada and Whitehead, 2007)	(Tunsaringkarn et al., 2014)	(Ciarrocca et al., 2012)
Location	Hong Kong, China	La Plata, Buenos Aires	Mexico, Mexico.	Bangkok, Thailand	Rome, Italy
Benzene	26.7	13.42	59	46.13	14.3
Toluene	77.2	18.90	256	91.10	34.9
Ethylbenzene	3.1	1.80	36	4.55	
P-Xylene	12.1	10.91	96	58.27	88.5
M-Xylene					
Pyridine					
O-Xylene	4.6	2.3	34		
Cumene					
Dipentene	0.2		74		
N-Propylbenzene					
Styrene	1.8				
P-Isopropyltoluene					
1,3,5 Trimethylbenzene			13		
1,2,4 Trimethylbenzene			42		
1,2,3 Trimethylbenzene			9		

And this fact, can be observed in the low differences between the initial and second home samples (paired t-test, $p<0.05$). Considering that the decay rate is exponential, large differences in concentrations are expected during the first days/ hours, after the remodelling is completed (Järnström et al., 2006, Liang et al., 2014).

However, most compounds measured in homes had higher concentrations during the second sampling compared to the initial sampling, which leads to the conclusion that in both cases (initial and second sample), VOC concentrations were more influenced by the human activities than from the construction products' emission rate.

Table V-15 VOC comparison between the new office and home (µg m^{-3}).

	Office	FIXAT	
	New office (first day)	New house (first year)	New house (second year)
Benzene	0.5	1.7	2.8
Toluene	167	25	17
Ethylbenzene	49	2.0	2.0
p-xylene	54	1.0	1.8
m-xylene	167	3.0	2.0
Pyridine	10	0.3	0.1
o-xylene	62	2.0	3.6
Cumene	1.6	0.2	1.1
Dipentene	16	47	4.0
N-propylbenzene	1.7	0.3	0.5
Styrene	1.7	2.0	1.3
p-isopropyltoluene	2.8	4.1	2.4
1,3,5-trimethylbenzene	1.4	0.6	1.6
1,2,4-trimethylbenzene	5.2	2.0	3.0
1,2,3-trimethylbenzene	2.5	0.8	2.0
Benzaldehyde	120	3.6	1.1
Octaldehyde	16	6.7	4.2
2-ethyl-1-hexanol	104	23	3.2
Naphthalene	1.2	1.3	0.6

5.4.7 Possible contributors base on the percentiles

For VOCs, the results point towards significant contribution from home and office microenvironments, since both of them were present in 90th percentile + and –. Differences in the 90th + percentile for some of the compounds were found across the microenvironments (Appendix 9). A major number of compounds were found for street microenvironments (which includes walk, bike or stand) rather than for the rest of the commute transports. Car compounds were similar to the street, however, compounds such cumene, dipentene, and thrimethylbenzenes were not observed at the 90th + percentile. Cars are more associated with BTEX compounds (Golhosseini et al., 2013) and higher concentrations were displayed for more volatiles compounds like

ethylbenzene, p,m, o-xylene and pyridine at bus transport mode, compounds that had been reported emitted higher concentration during the bus commute (Lau and Chan, 2003, D'Souza et al., 2009), while for train, the opposite trend was present; displaying the higher concentration in the less volatile compounds such cumene, dipentene, n-propylbenzene, thrimetylbenzenes, octaldehyde, benzaldehyde, 3-vynilpyriridine and naphthalene. According to the EPA, 1999 one of the primary sources of cumene are; solvent, plastic, cigarette and motor vehicles (Foureman, 1999). Dipentene sources possible in trains could be the cleanning products, fragrances and paints (Falk Filipsson et al., 1998, Park and Ikeda, 2006, Shin and Jo, 2013) (Table V-16).

VOC in restaurant and pubs show high concentrations of compounds such benzene, styrene and benzaldehyde normally found in high concentrations while subjects cook (Huang et al., 2011). Additionally, restaurants also displayed a high concentration of compounds like cumene, pyridine, dipentene, styrene, 3-vinylpyridine and naphthalene. The rest of the compounds appeared only the 90^{th} - percentile. Compounds sources are associated with traffic and products emissions (Edwards et al., 2001), construction products (Hayashi and Osawa, 2013)

Shops and other microenvironments show differences, and while more compounds were registered in the 90^{th} + percentile for shops than in other indoor environments, most species were found in the 90^{th} - percentile. The outdoor environments show that most of the compounds registered in high concentrations were while subjects spent time in the park compare with the garden. Petrol station concentrations were particularly registered in the 90^{th} - percentile.

Table V-16 Correlation between the subject's activities and the VOC 90th + percentile concentrations.

Locations	Benzene	Toluene	Ethylbenzene	p-xylene	m-xylene	cumene	pyridine	o-xylene	dipentene	n-propylbenzene	1,3,5-Trimethylbenze	styrene	p-isopropyltoluene	1,2,4-Trimethylbenze	Octylaldehyde	1,2,3-Trimethylbenze	2-ethyl -1-hexanol	Benzaldehyde	3-vinylpyridine	Naphthalene
Home	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Living room	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Kitchen	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Office	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x
Lab	x					x				x	x	x		x						x
Common room	x	x				x	x		x	x	x	x	x	x		x	x		x	x
Other office		x	x	x	x		x	x	x	x	x			x	x		x	x	x	
Street	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Car	x	x	x	x	x		x	x		x		x		x	x		x	x	x	x
Car park	x					x					x					x				
Bus			x	x	x		x	x										x	x	
Bus stop							x						x					x	x	
Train	x					x			x	x	x			x	x	x		x	x	x
Train station									x	x	x			x	x	x		x		
Restaurant	x					x	x		x			x				x		x	x	x
Pub	x											x						x		
Shop	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x		x
Gym			x	x	x			x		x	x			x						
Other indoor	x	x										x						x		
Park			x	x	x			x	x	x	x		x	x	x		x			
Garden	x	x				x						x				x				x
Petrol station																				
Other outdoor		x										x								x

5.5 Conclusion

Under the ambient conditions and the socioeconomic characteristics of the sampling population, it was observed that the higher concentrations were observed in office microenvironments. Most of the sampling volunteers had their offices at the University of Birmingham where work construction was taking place while the sampling campaign was in progress. The influence of outdoor concentration over the indoor and personal exposure was observed. First year concentrations from group two (recently remodelled house) exceed the values obtained for group three (control group) during the same year, mostly for compounds such as: toluene, dipentene, n-propylbenzene, styrene and benzaldehyde. However, the differences were observed for personal and office microenvironment, while increment in concentrations, because houses were new or recently redecorated were not found significantly high compared with old houses. Possible reason can be observed when group two first sample and second sample were analysed in which the concentrations in a specific house were similar to that obtained from the same house but after a year, except for dipentene which was higher for recently remodelled houses (group two). And by comparing the new a recently remodelled office (Chapter IV) with the FIXAT concentrations, recently redecorated offices were found to have higher concentrations than those observed in new houses for FIXAT cohort. Sampling time might influence the concentration as the FIXAT samples were collected during the first three months of the construction or redecoration, while office samples were collected within a few days after the redecoration.

Based on the 90^{th} percentile analysis, major contributors to the high air pollutant exposure were commuting and street activities such walking and biking. The risk of

exposure to air pollutants can be similar considering only the ambient conditions, although the exposure tends to vary based on the location and activity. Therefore, personal exposure measurements are required to accurately establish the relationship between activity and compound concentrations for use in epidemiologic studies. Everyday activities can be predicted as average concentration, and did not vary significantly between subjects. However, the risk increases with activities that are not performed frequently, or by everyone. Further investigation need to be done considering those microenvironments in which subjects spent less than 30 min. and those that were visited for 1 or 2 subjects as results are only for references and those cannot represent the entire sampled population.

CHAPTER VI. CONCENTRATION OF $PM_{2.5}$, PAHS AND OXY-PAHS

6.1 Introduction

People spend most of the time (60-80 %) in indoor microenvironments, in which a wide range of air pollution sources can be identified (Lim et al., 2012, Harrison et al., 2009). It is complex to determine the health risks of PM exposure due to the highly variable composition and size of the particles. Therefore, to evaluate the risks it is fundamental to have more information in regards to the composition considering the sources (Hodas et al., 2014). Previous studies have shown poor correlation of $PM_{2.5}$ between local site and personal exposure with the central sampling site (Anastasopoulos et al., 2012, Hodas et al., 2014, Brokamp et al., 2015), indicating that the level of exposure can be underestimated when it is calculated by using the central site monitors.

PAHs and oxy-PAHs have been reported to be bound to PM, mostly in the $PM_{2.5}$ size fraction (Anastasopoulos et al., 2012, Choi et al., 2012, Martellini et al., 2012, Cochran et al., 2012, Ringuet et al., 2012, Bandowe et al., 2014), and often show high variability at the local scale (Hänninen et al., 2013, Barrado et al., 2013). These compounds are especially studied because of their carcinogenic/mutagenic proprieties, and within this class of compounds, PAH derivatives have been reported to be more toxic. Higher toxicity in the case of derivatives is attributed to their direct mutagenic potency, since PAH typically require enzymatic activation (1983, Ang et al., 1987, Wei et al., 2012).

6.2 Objectives

To determine the correlation of $PM_{2.5}$ considering the reported difference between fixed sampling sites with home and personal exposure concentrations, as well as the traditional gravimetric lab method (integrated filter) with online concentrations obtained from the MicroPEM^{TM}

To determine the personal exposure to PAHs and oxy- PAHs considering the activities performed by the volunteers.

To assess the possible sources of the compounds based on spatial and temporal variations.

6.3 Methodology

6.3.1 $PM_{2.5}$, PAHs, and Oxy-PAHs sampling collection

Subjects and sampling criteria was described in CHAPTER V. However, or this section data from the filters was used without considering the sampling groups. Therefore data from group 2 and 3 was considered as our total sampling population. And this is because the effect of new or recently remodelled houses will no influence the concentration of $PM_{2.5}$, PAHs and oxy PAHs.

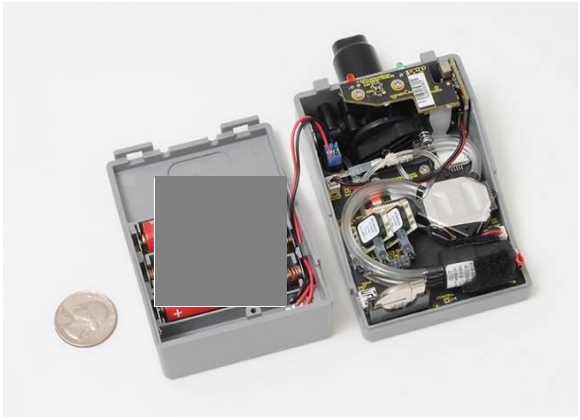
24-hour PM samples were collected on 47 mm borosilicate glass microfiber filters (VWR- Emfab™), woven glass cloth and bonded with PTFE using a Casella (Apex) pump which operated at a flow rate of 3 L min^{-1}. In order to collect particles smaller than the cut size of 2.5 µm (aerodynamic diameter), a 2.5 µm Teflon-coated personal sampling aluminium cyclone was used. Filter samples collected using this set-up were used for analysis of $PM_{2.5}$, PAHs and Oxy-PAHs.

6.3.1.1 $PM_{2.5}$

$PM_{2.5}$ mass concentrations were obtained from the gravimetrical analysis, using a Sartorius MCS microbalance. The filters were conditioned for 24 hours at 25 °C and 40 %RH; and weighed before and after sampling. To eliminate the effect of static electricity, an ionizing blower and a α-particle source (^{210}Po) was used. After gravimetric analysis, filters were stored in the freezer at -20 ºC until chemical analysis was conducted.

During the study period, $PM_{2.5}$ concentrations from the central site in Birmingham were obtained through the DEFRA archives. The selected ambient sampling site was Birmingham Tyburn (UKA00479), which is classified as an urban background site. The monitoring station was within a self-contained, air-conditioned housing located on the south side of the A38.

Subjects were also equipped with a prototype monitor (MicroPEM^{TM}), developed by RTI international and Columbia University, which collects $PM_{2.5}$ on a Teflon filter and provides real time PM concentration using a 780 nm nephelometer for a 10 s average period (Rodes et al., 2012, Rodes et al., 2010) (Picture VI-1).



Picture VI-1 Prototype RTI MicroPEM ™

The ambient concentrations were used for comparison with the FIXAT filter samples and sensor results. The historical archives from the DEFRA data base were selected based on the volunteers' sampling dates and times.

6.3.1.2 PAHs and Oxy-PAHs

The filters were solvent extracted using HPLC grade dichloromethane (DCM) for PAHs and oxy-PAHs following the standard operation procedures used in the MATCH project for PAH analysis (Harrison et al., 2009).

Briefly, the filters were injected with 50 µl of oxy-PAHs internal standard and 50 µL of PAH internal standard. Subsequently, 10 mL of DCM HPLC grade was added and the organic matter was extracted in the ultrasonic bath for 25 minutes at 30 °C. To eliminate impurities, the extract was filtered using a chromatography column, composed of anhydrous Na_2SO_4 and pre- cleaned glass wool. The following step was to concentrate the samples from around 10 mL to less than 1 mL by blowing clean N_2 into the sample. The samples were subsequently transferred to GC vials and further concentrated to 100 µl. Finally, the samples were transferred into the insert vials and concentrated until they were almost dry. The sample was subsequently reconstituted by adding 10 µl of p-terphenyl-d14 and 10 µl of 2-fluoro- 7 nitrofluorene for oxy-PAHs. The solvent was changed from DCM to nonane adding 30 µl to prepare a final volume of 50 µl. The samples were stored in -20°C freezer until analysis.

The PAHs analytical method used in this study was developed by and used in the MATCH project (Harrison et al., 2009). The main parameters are enlisted in Table VI-1. An Agilent Technology system (9890N) was used to separate and analyze PAHs using a capillary column from Agilent Technology (19091s-433). Table VI-2 shows the monitored masses with the retention time of the PAHs and the abbreviations used.

Table VI-1 GC-MS conditions for PAHs.

	PARAMETERS	CONDITIONS
GC	Initial temperature	100˚C
	Maximum temp	325˚C
	Initial time	2 min
	Equilibration time	0.50 min
	Post temp	0
	Post time	0
	Run time	62 min
MS	Carrier gas	Helium
	Mode	Split

Table VI-2 Target natural compound for PAHs.

COMPOUND	ABBREVIATIONS	RETENTION TIME (MIN)	TARGET ION ($M^{+)}$	QUALIFIER ION
Naphthalene	Naph	6.7	128	127
Acenaphthylene	Ac	13.3	152	151
Acenaphthene	Ace	14.2	153	154
Fluorene	Fl	16.9	166	165
Phenanthrene	Ph	21.9	178	176
Anthracene	An	22.2	178	176
Fluoranthrene	Fluo	28.9	202	200
Pyrene	Pyr	30.1	202	200
Benzo(a)anthracene	B[a]A	37.2	228	226
Chrysene	Chry	37.4	228	226
Benzo(b)fluoranthene	B[b]F	43.0	252	250
Benzo(k)fluoranthene	B[k]F	43.2	252	250
Benzo(e)pyrene	B[e]P	44.3	252	250
Benzo(a)pyrene	B[a]P	44.5	252	250
Indeno(1,2,3-cd)pyrene	I[1,2,3-cd]P	49.6	276	274
Dibenz(a,h)anthracene	D[a,h]A	49.9	278	276
Benzo(ghi)perylene	B[ghi]P	50.6	276	274
Coronene	Cor	57.4	300	298

Oxy-PAHs were analysed using a Gas Chromatography (6890N Agilent Technology) and 5973 inert mass selective detector running in negative-ion chemical ionization. Samples were placed in a Gerstel MPS 2 injector which takes 1 µL injection into the GC column (Agilent DB-5MS UI). The instrument control parameters are described in Table VI-3. The monitored masses for oxy-PAHs are show in Table VI-4.

Table VI-3 GC-MS conditions for Oxy-PAHs.

	PARAMETERS	CONDITIONS
Oven	Initial temperature	30˚C
	Maximum temp	350˚C
	Initial time	5 min
	Equilibration time	0.50 min
	Post temp	0
	Post time	0
	Run time	92.50 min
MS	Carrier gas	Helium
	Mode	Split

Table VI-4 Target natural oxy-PAHs compounds.

COMPOUND	ABBREVIATION	RETENTION TIME (MIN)	TARGET ION ($M^{+)}$
1,4-Naphthoquinone	1,4NQ	35.15	158
2,6-di-tert-butyl-1,4-benzoquinone	2,6-DTBQ	36.42	220
2-methyl-1,4-naphthoquinone	2MNQ	38.50	172
Acenphthoquinone	AceQ	51.29	208
Anthraquinone	AQ	54.44	222
2-methyl-anthraquinone	2MAQ	54.46	208
2,3-dimethyl-anthraquinone	2,3DMAQ	58.28	236
7,12Benz[a]anthracenequinone	7,12BaAQ	64.76	258
5,12-naphthacenequinone	5,12NAQ	66.48	258

6.4 Results

6.4.1 $PM_{2.5}$, PAHs and Oxy-PAHs study population

$PM_{2.5}$, PAH and oxy-PAHs analysis was done for subjects recruited for group two and three as group one were only tested for VOC. During the sampling campaign not all the volunteers were able to allow the sampling equipment in their office, because of the lack of authorization, and as a result only ~50 % subjects had workplace samples. Only the first year sample from group two and three was considered for the statistical analysis of this chapter, as year two was collected only for group two (Table VI-5).

Table VI-5 Total number of samples taken per microenvironment split by groups.

	PAHs	Oxy-PAHs	$PM_{2.5}$
Group 2/3	2/3	2/3	2/3
Persona (PE)	16/18	17/17	17/17
Home (H)	16/18	17/17	17/17
Work (W)	8/8	8/8	7/9
Total	40/44	42/42	41/43

The data was tested for normality resulting in a positive-skewed distribution for $PM_{2.5}$, PAHs and oxy-PAHs. As a result, the values were $\log_{10}$ transformed for conducting

comparisons, and Geometric mean (GM) and geometric standard deviation (GSD) were reported. The sampled concentrations were characterized by using descriptive statistics. In each group two duplicated samples were taken for personal and home exposure.

The online sensor samples were obtained for some of the PE volunteers, however, not all the data was used because of the internal error observed in the sensor, in which timestamp was lost or automatically reset to the default when the instrument lost power. Also negative and zero values were obtained from some samples, and deleted. However the samples with most of the sampling period that registered negative values were eliminated from the study, in most of the cases, the 15 seconds averaging sampling time showed more negative values than the 10 s. Table VI-6 shows information about $PM_{2.5}$ and the number of samples used to identify the correlations. Filters from FIXAT were used from subjects with either $PM_{2.5}$ sensor or with data available on the fixed site.

Table VI-6 Number of samples used from the sensor and the fixed site.

	$PM_{2.5}$ Sensor	**$PM_{2.5}$ Fixed site**
Personal (PE)	11	42
Home (H)	12	44

6.4.2 Comparison of $PM_{2.5}$ concentrations from integrate filter, sensor and central sites

The integrated 24 hours concentrations on the filter (FIXAT samples group two and three) were compared with the measurements taken using the MicroPEM^{TM} sensor

which was co- located with the filter pump during PE sampling (Figure VI-1). 23 % of the FIXAT volunteers were sampled by using the sensor.

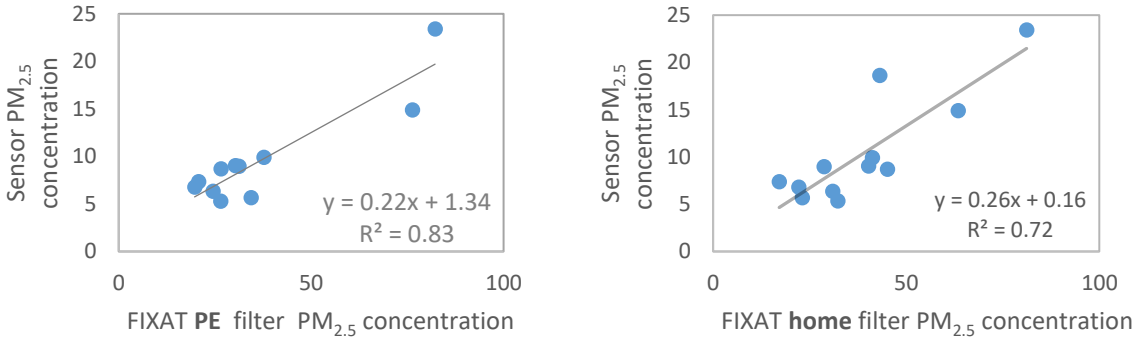


Figure VI-1 Relationship between $PM_{2.5}$ concentrations from the FIXAT filter and the Micro PEM™ sensor (N=11) personal exposure and home data.

The results show a positive good correlation between the two different methods used to measure $PM_{2.5}$ in the PE data, obtaining R^2 values of 0.83 and 0.72 for home comparison. However, the sensor underestimated the concentration compared to the filter. Therefore, sensor data can be corrected by using the regression equation considering high concentration microenvironments as the intercept line does not reach zero.

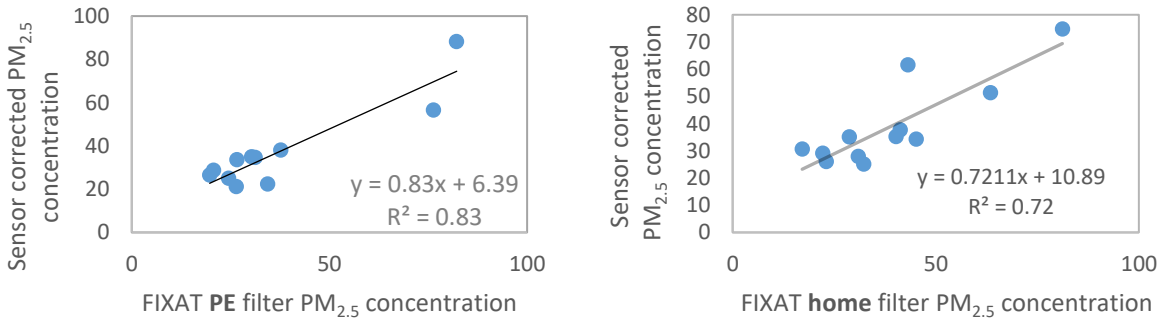


Figure VI-2 Relationship between $PM_{2.5}$ concentrations from the FIXAT filter and the Micro PEM™ sensor corrected data using the regression equation given in Figure VI-1 (N=11) personal exposure and home data.

The corrected data from PE and home sensor data can be observed in Figure VI-2, in which the square root value was the same as the plots in Figure VI-1. However, the concentrations values increased.

The regression equation was used to correct the sensor data and compared the values with the central site data obtained during the same sampling day. The results show a good correlation (R^2= 0.75) using the PE sensor data. However the home sensor data showed poor correlation with the central site values (R^2= 0.45) (Figure VI-3).

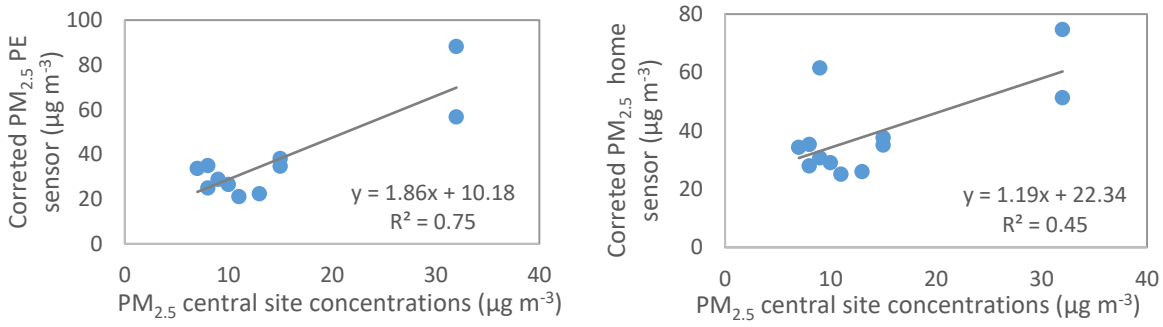


Figure VI-3 Relationship between $PM_{2.5}$ concentration from de central site and the corrected sensor Micro PEM™ (N=12) Personal exposure and home.

Central site $PM_{2.5}$ concentrations were also compared against the $PM_{2.5}$ data generated from the lab method (FIXAT filters) (Figure VI-4). The relationship between PE and home with the central sites concentrations was found to be weak showing an R^2 equal to 0.32. The Pearson correlation value was 0.56 for both and the results showed statistical differences (paired t-test, $p< 0.05$). It was observed that higher values were obtained by using the gravimetric method than those obtained from the DEFRA data. These results were in agreement with recent findings about the low relationship between ambient and PE concentrations of $PM_{2.5}$ (Balmes et al., 2014, de Hartog et al., 2010, Michikawa et al., 2014, McAuley et al., 2010). Moreover, indoor concentration were also found to be different than the PE (R^2=0.40), confirming that

central site monitoring stations and indoor concentration do not accurately reflect the personal exposure. These are good indicators of the overall population exposure but not a good estimator of the individual risk, which takes particle composition into account.

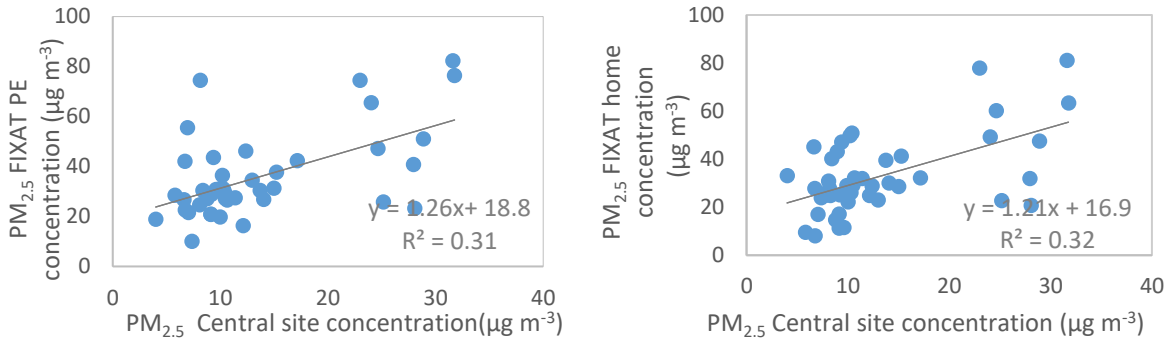


Figure VI-4 Relationship between the $PM_{2.5}$ concentrations from the FIXAT filter and the ambient concentrations DEFRA in µg m^{-3}, a) personal exposure (N=43), b) home (N= 44).

Possible reasons that could influence the differences include; the relative distance between the indoor and ambient sampling sites (Chen and Zhao, 2011, Quang et al., 2013), location of the house (background or traffic street) (Dos Santos-Juusela et al., 2013, Fischer et al., 2000) and the insulation of the house (Gens et al., 2014).

6.4.3 Concentration compared with the subject main characteristics

Personal exposure, home and work microenvironments were sampled. Statistical analysis was done using SPSS 21, considering only the first sample for group two and three. Because the number of samples was not similar, a one way ANOVA model with a sum of squares type III and Tukey test was used to estimate any difference between variables and was applicable for analysing compound by compound.

6.4.3.1 $PM_{2.5}$

Higher $PM_{2.5}$ concentrations were reported at work (35 µg m^{-3}) followed by PE (32 µg m^{-3}). However, the maximum value was registered at home microenvironment (152 µg

m^{-3}). No statistical difference was observed between the sampling locations (one way ANOVA $p>0.05$). Home and work concentrations were higher than the recommended values proposed by the EPA (35 µg m^{-3}) and the three sampling sites' concentration exceeded the WHO and EC (25 µg m^{-3}) (Table VI-7). However, PE exposure is composite partially from the home and work microenvironments. Therefore, even if most of the time was spent at home, subjects were exposed to part of the $PM_{2.5}$ concentration as lower PE concentration were obtained.

Table VI-7 $PM_{2.5}$ concentration from the FIXAT samples (µg m^{-3}).

Sample type	Mean	SD	Min	Max	GM
PE (N= 34)	37	25	10	146	32_a
Home (N=34)	34	25	8.0	152	29_a
Work (N=16)	45	33	11	125	35_a

Same letter indicates concentrations with no statistical difference for a one way ANOVA ($p>0.05$)

$PM_{2.5}$ concentrations for PE were similar to the concentrations reported in North Carolina (US) (Wallace et al., 2006) and Athens (Greece) summer concentrations (Georgiadis et al., 2001), but much lower than those reported in Italy (Borgini et al., 2011) and China (Du et al., 2012, Jahn et al., 2013). $PM_{2.5}$ home concentrations were almost similar to the values obtained Athens (Greece) (Diapouli et al., 2010), North Carolina (US) (Wallace et al., 2006), Tokyo (Japan) (Michikawa et al., 2014) and Leipzig Germany (Franck et al., 2011). For work place, the values obtained had similarities with the concentrations reported for Athens (Diapouli et al., 2010) and North Carolina, US (Wallace et al., 2006) and much lower than those reported for China (Du et al., 2010).

6.4.3.2 PAHs and oxy-PAHs

In general, average concentrations of PAHs were in accordance with the reported values in (Harrison et al., 2009), (Saborit et al., 2009), (Aquilina et al., 2010) and (Alam et al., 2013b) for UK and Birmingham. Average PE, home and work microenvironments concentrations for PAHs and Oxy-PAHs are summarized in Table VI-8. No statistical difference was reported for most of the PAHs and Oxy-PAHs at the microenvironments (ANOVA, $p>0.05$). However, a statistical difference was observed for compounds such acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene and coronene, with higher values reported at work microenvironment.

Two possible reasons for the high concentration at the work microenvironments can be discussed; first, most of the volunteers worked at the University of Birmingham and during the sampling period, several construction activities took place around the campus. It is considered that during the construction, not only the workers but also the buildings near to the site are exposed to PAHs, bounded in $PM_{2.5}$. The main reason for this is that at the surroundings, construction activities such as the transport of the materials, accumulation of waste materials, heavy engines and vehicles, and new pavement and foundations will release dust or pollutant gases (Kong et al., 2015).

Second, during the years 2011 and 2012, Birmingham had the hottest summers compared with previous years, therefore offices windows were opened during the working days. High infiltration factors of particles has been reported for buildings where the windows are open (Rim et al., 2013). It has also been reported that up to 50 % of the outdoor PM can penetrate indoors, and less than the 25 % of the indoor particles are generated from the indoor sources (Sangiorgi et al., 2013, Yan et al., 2015), which will lead to high concentration of PAHs, which normally are found in the PM_{25} samples.

Extreme values (max) were observed for phenanthrene, benzo(a) anthracene, for home and work while benzo(e)pyrene and benzo(a)pyrene was observed to be high in the three microenvironments. These compounds had been reported to be present during road construction (Greenspan et al., 1995). Although most of the compounds were close to the LODs, it can be observed that the maximum values are far from the LOD. For instance, the most abundant compound was benzo(a)pyrene registered GM concentration for PE, home and work of 0.46, 0.43 and 0.31 ng m^{-3} respectively.

Studies have reported that as much as 70 % of the indoor concentration of PAHs can be attributed to outdoor sources, and together with the presence of indoor sources, leads to even higher concentrations (Choi and Spengler, 2014).

In general, PE and indoor (home and work) concentration were similar to previous studies conducted in Birmingham (Saborit et al., 2009, Harrison et al., 2009, Aquilina et al., 2010, Delgado-Saborit et al., 2011b). However the concentrations were higher or almost similar to the outdoor levels reported by (Alam et al., 2013a) and (Delgado-Saborit et al., 2013) except that this study registered higher concentration for benzo(a)pyrene. Higher values were reported by (Alam et al., 2013b) for compounds such phenanthrene, fluoranthene and pyrene which are reported to be indicators of traffic sources.

Oxy-PAHs personal exposure and indoor concentration have not been previously reported. The ANOVA tests did not find any statistical difference between the microenvironments (one-way ANOVA $p>0.5$).

Table VI-8 Particle PAHs and oxy-PAHs average concentration in ng m^{-3}

Compounds	Personal exposure (N=34)					Home (N=34)					Work (N=17)				
PAHs	AM	SD	Min	Max	GM	AM	SD	Min	Max	GM	AM	SD	Min	Max	GM
Naphthalene	1.10	1.09	0.02	4.46	**0.39a**	1.22	1.35	0.02	7.25	**0.60a**	2.87	2.79	0.02	9.03	**1.03a**
Acenaphthylene	BDL	0.13	BDL	0.60	BDL	BDL	0.10	BDL	0.37	BDL	BDL	0.56	BDL	2.35	BDL
Acenaphthene	0.19	0.13	0.02	0.59	**0.16a**	0.19	0.15	0.08	0.90	**0.16a**	0.59	0.40	0.02	1.39	**0.39b**
Fluorene	0.25	0.17	0.08	0.98	**0.21a**	BDL	0.12	BDL	0.65	BDL	0.50	0.29	0.04	1.12	**0.41b**
Phenanthrene	0.80	0.81	0.13	4.54	**0.61a**	0.71	0.45	0.24	2.58	**0.60a**	1.51	0.97	0.16	3.00	**1.17b**
Anthracene	BDL	0.12	BDL	0.50	BDL	BDL	0.09	BDL	0.39	BDL	BDL	0.26	BDL	0.96	BDL
Fluoranthrene	BDL	0.29	BDL	1.27	BDL	BDL	0.13	BDL	0.66	BDL	0.50	0.35	0.05	1.20	**0.38b**
Pyrene	BDL	0.32	BDL	1.55	BDL	BDL	0.30	BDL	1.83	BDL	0.77	0.57	0.06	2.38	**0.53b**
Benzo(a)anthracene	0.23	0.37	0.07	2.23	**0.16a**	0.15	0.06	0.07	0.29	**0.14a**	0.27	0.19	0.00	0.59	**0.16a**
Chrysene	0.32	0.22	0.00	0.99	**0.24a**	0.32	0.15	0.09	0.68	**0.29a**	0.49	0.36	0.08	1.12	**0.37a**
Benzo(b)fluoranthene	0.27	0.17	0.10	0.78	**0.23a**	0.24	0.15	0.10	0.71	**0.21a**	0.32	0.25	0.01	0.99	**0.22a**
Benzo(k)fluoranthene	0.19	0.14	0.01	0.66	**0.15a**	0.19	0.14	0.05	0.71	**0.16a**	0.27	0.27	BDL	0.80	**0.15a**
Benzo(e)pyrene	0.33	0.59	0.00	3.50	**0.13a**	0.28	0.35	0.00	2.06	**0.14a**	0.54	1.07	BDL	4.54	**0.11a**
Benzo(a)pyrene	1.32	1.59	0.01	6.05	**0.46a**	1.31	1.48	0.01	5.48	**0.43a**	1.56	1.92	0.01	5.00	**0.31a**
Indeno(1,2,3-cd)pyrene	0.21	0.18	0.01	0.80	**0.15a**	0.18	0.13	0.06	0.58	**0.16a**	0.27	0.24	0.03	0.78	**0.19a**
Dbenz(a,h)anthracene	0.10	0.08	0.02	0.38	**0.08ab**	0.08	0.05	0.03	0.29	**0.07a**	0.16	0.15	0.02	0.68	**0.12b**
Benzo(ghi)perylene	0.29	0.23	0.04	1.06	**0.23a**	0.29	0.18	0.07	0.86	**0.25a**	0.34	0.22	0.05	0.92	**0.28a**
Coronene	0.28	0.13	0.10	0.55	**0.26a**	0.29	0.13	0.15	0.61	**0.27a**	0.69	0.49	0.04	1.81	**0.52b**
Oxy-PAHs															
1,4-Naphthoquinone	0.38	0.22	0.05	0.92	**0.33a**	0.26	0.05	0.05	0.41	**0.25a**	0.32	0.27	0.05	1.33	**0.27a**
2-methyl-1,4-naphthoquinone	BDL	0.47	0.48	BDL	BDL	BDL	0.02	BDL	0.59	BDL	BDL	0.57	BDL	2.80	BDL
Acenaphthenequinone	0.92	0.71	0.05	2.60	**0.57a**	0.55	0.34	0.05	1.09	**0.33a**	0.56	0.34	0.05	1.14	**0.35a**
9,10 anthraquinone	1.68	1.89	0.13	8.99	**1.16a**	BDL	0.20	BDL	1.19	BDL	BDL	0.75	BDL	3.78	BDL
2-methyl-anthraquinone	1.77	2.55	0.12	15.3	**1.22a**	1.45	2.55	0.12	13.4	**0.94a**	BDL	0.89	BDL	4.38	BDL
2,3-dimethyl-anthraquinone	1.12	0.70	0.06	2.78	**0.93a**	0.99	1.22	0.68	7.86	**0.83a**	0.95	0.80	BDL	3.98	BDL
Benz(a)anthracene 7,12-quinone	1.19	1.21	0.18	7.15	**0.93a**	0.84	0.54	0.18	3.21	**0.75a**	2.43	7.08	0.14	29.8	**0.84a**
5,12-naphthacene-quinone	1.13	2.50	0.09	11.9	**0.24a**	0.48	0.61	0.09	2.85	**0.24a**	0.48	0.57	BDL	1.91	**0.27a**

ANOVA ($p < 0.05$) has been used to test for statistically different concentrations between sampling sites. Numbers shown in bold were statistically different as indicated by the different letters associated with each. For the concentrations in normal font, there was no significant difference.
BDL- below detection limit

The maximum detected concentrations were for 9, 10-anthraquinone with 8.9 ng m^{-3} for PE, 2-methyl-anthraquinone registered the maximum values at PE and home with 15.34 and 13.46 ng m^{-3} respectively; and benz(a)anthracene 7, 12-dione for work location (29.8 ng m^{-3}). For 2-methyl-1,4-naphthoquinone 9, 10-Anthraquinone and 2-methyl-anthraquinone registered AM or GM concentrations below the limit of detection. However, the maximum obtained values were mostly for work microenvironment.

Comparing the results with previous outdoor levels, PE and indoor levels of oxy-PAHs were higher than those previously reported for outdoors in Birmingham (UK) (Delgado-Saborit et al., 2013, Alam et al., 2013b, Alam et al., 2013a). However, it has been noticed that a higher concentration in the vapour phase for oxy-PAHs with MW lower than 208 Da, while the particle samples had registered higher concentration for compound with MW higher than 208 Da. (Alam et al., 2013b, Alam et al., 2013a). This pattern was also observed in our results. Therefore, we can conclude that oxy-PAHs with higher polarities may introduce an increment in the tendency of partition into the particulate phase (Alam et al., 2013a, Delgado-Saborit et al., 2013). Although the FIXAT oxy-PAH concentrations were higher than the outdoor level reported for Birmingham UK, these are lower than the values obtained in urban and rural areas in Beijing, China for 9,10 anthraquinone. However, maximum values obtained were similar to those reported in China. Benz(a)anthracene 7,12-quinone concentration was higher in this study, which is reported to be dominant in particulate phase (Li et al., 2015b).

The FIXAT concentrations were almost similar to the values reported from Santiago de Chile (Sienra, 2006) and in France (Albinet et al., 2007, Ringuet et al., 2012). 9,10-Anthraquinone, 2-methyl-anthraquinone, 2.3-Dimethyl-anthraquinone and

Benzo(a)anthracene7,12-dione were the most abundant compounds (Tsapakis and Stephanou, 2007). The 9,10-Anthraquinone concentrations PE (1.2 ng m^{-3}) were similar to those reported by (Souza et al., 2014) (1.1 ng m^{-3}) value obtained by measuring the sugar cane burning. Indoor concentration reported by (Ding et al., 2012) for China were by far higher than the obtained in this study.

Relative low mean concentration of PAHs and oxy-PAHS were obtained from Birmingham UK samples. However, extreme values observed in this study concentrations can be explained by the exposure to traffic emissions (Li et al., 2015b). Since most of the higher concentrations were associated with PE and work microenvironment; where there was a significant amount of construction work. A possible source at home, which influences the high values obtained for PE can suggest at kitchen exposure (Ding et al., 2012).

6.4.4 Characterization of the concentrations

6.4.4.1 Gender difference

Considering the main characteristics obtained by the questionnaires, subjects' concentrations were analysed to estimate possible sources of PAHs and oxy-PAHs. Gender differences was observed for high molecular compound such indeno (1,2,3-cd) pyrene, Dibenz(a,h)anthracene, Benzo(ghi)perylene and Coronene which concentration were higher in female subjects (independent t-test $p>0.05$) (Appendix 10).

It has been observed in previous studies that traffic emission are more related with LMW compounds, which are more vulnerable to atmospheric processing as they are less stable (Alam et al., 2013b). Therefore, HMW compounds are reported to be more stable, because the characteristic of vapour –particle partitioning are easier to detect

those in the particle phase (Alam et al., 2013a, Anastasopoulos et al., 2012, Bandowe et al., 2014, Kliucininkas et al., 2011). Even though all subjects were exposed to traffic sources, the observed gender difference might indicate that female subjects were exposed to other sources of emission during the day-to-day activities that might include for instance cooking.

6.4.4.2 Seasonal variations

As previously mentioned in the methodology, equal number of subjects for the seasonal sampling was challenging as we depend on the subjects availability and decoration time. However, we made an effort to collect samples during hot and cold seasons. PAH concentrations showed a statistically significant difference between seasons for compound such benzo(a) anthracene during the personal exposure measurements with 0.12 ng m^{-3} for the hot and 0.20 ng m^{-3} during the cold period. Home concentration shows statistical differences for compounds like benzo (a) anthracene, Chrysene and coronene showed higher concentration during the cold season. For work concentration chrysene was the only compound that showed seasonal variation with higher values during the cold season. Clearly higher values were observed during cold season.

No statistical differences between the two variables for oxy-PAHs in PE and home (Independent t-test $p>0.05$) except for 5,12-naphthacene-quinone at the work microenvironments, for which the concentration was observed to be higher during the cold season (0.34 ng m^{-3} compared to 0.09 ng m^{-3} in the hot season) (Appendix 11). Possible gas/particle partition of the compound could occur because of the influence of temperature during the winter in the indoor microenvironments (Bandowe et al., 2014). Kitchen concentration were also reported for China with lower concentration

during the winter compared to the summer; this is attributable to high ventilation. Moreover, high winter concentrations can be a result of secondary formation (Ding et al., 2012).

6.4.4.3 Transport mode

Different transport modes for home –work journey were reported, and one way ANOVA test with type III errors was used in PE data from year one to identify any difference between transport modes for all the compounds. According to the TAD, subjects using bus or train also walk, subjects who reported not to work used multiple transport modes during the day, and therefore, they were categorized as multiple transport. Most of the compounds were observed to be statistically similar except for acenaphthylene, acenaphthene, anthracene and benzo(e)pyrene reporting a higher concentration in bus commute mode, while higher concentration of benzo(k) fluoranthene and benzo(e)pyrene was reported for car transport (Table VI-9). However, considering the extreme values, 9th percentile concentration were observed only for subjects that walk as not 90th percentile was observed for the rest of the transport modes (Appendix 12). In general, higher concentration was obtained for compounds such phenanthrene and pyrene in transport mode (~ 1 ng m^{-3}). However, those are lower than the previous concentrations reported for traffic and background road in Birmingham UK which ranged between 1.5 and 3 ng m^{-3} (Alam et al., 2013b) and in Beijing, China (Wu et al., 2014). Interestedly, the results are close to those obtained by (Delgado-Saborit et al., 2013). Oxy-PAHs results show concentration higher than the reported by (Alam et al., 2013b) and (Delgado-Saborit et al., 2013) in which most of the values were lower than 0.3 ng m^{-3}, while this study registered values ≥ 1.01 ng m^{-3}.

Table VI-9 FIXAT transport mode concentrations (ng m^{-3}).

	Multiple (N=4)					Car (N=5)					Train (N=6)					Bus (N=3)					Cycle (N=5)					Walk (N=12)				
	AM	SD	Min	Max	GM	AM	SD	Min	Max	GM	AM	SD	Min	Max	GM	AM	SD	Min	Max	GM	AM	SD	Min	Max	GM	AM	SD	Min	Max	GM
Naphthalene	1.84	1.26	0.68	3.56	1.53	0.95	1.21	0.02	2.96	0.22	0.99	0.66	0.02	2.08	0.55	0.84	1.33	0.02	2.37	0.17	0.36	0.48	0.02	0.89	0.08	1.25	1.27	0.02	4.46	0.58
Acenaphthylene	0.04	0.04	0.01	0.08	**0.03a**	0.15	0.13	0.00	0.29	**0.07ab**	0.10	0.09	0.01	0.26	**0.07ab**	0.32	0.27	0.07	0.60	**0.23b**	0.15	0.12	0.01	0.33	**0.09ab**	0.11	0.09	0.01	0.25	**0.07ab**
Acenaphthene	0.15	0.05	0.10	0.22	**0.15a**	0.13	0.09	0.02	0.27	**0.10a**	0.13	0.04	0.07	0.17	**0.12a**	0.54	0.29	0.24	0.83	**0.48b**	0.30	0.18	0.17	0.59	**0.27ab**	0.19	0.12	0.10	0.54	**0.16a**
Fluorene	0.28	0.06	0.21	0.35	0.27	0.24	0.25	0.09	0.68	0.17	0.22	0.10	0.12	0.34	0.20	0.47	0.45	0.15	0.98	0.34	0.18	0.09	0.08	0.30	0.16	0.22	0.09	0.09	0.35	0.20
Phenanthrene	0.83	0.10	0.74	0.93	**0.82a**	0.91	1.00	0.29	2.67	**0.64ab**	0.75	0.45	0.29	1.52	**0.64ab**	1.88	2.32	0.26	4.54	**0.99b**	0.45	0.25	0.13	0.81	**0.38a**	0.59	0.31	0.24	1.15	**0.52ab**
Anthracene	0.11	0.05	0.04	0.16	0.10	0.13	0.17	0.03	0.42	0.08	0.13	0.11	0.01	0.29	0.08	0.32	0.19	0.12	0.50	0.27	0.12	0.06	0.04	0.17	0.10	0.10	0.10	0.01	0.37	0.05
Fluoranthrene	0.31	0.06	0.25	0.38	0.30	0.39	0.34	0.11	0.82	0.28	0.42	0.43	0.13	1.27	0.31	0.55	0.60	0.12	1.23	0.35	0.17	0.07	0.10	0.26	0.16	0.21	0.09	0.10	0.43	0.20
Pyrene	0.36	0.05	0.32	0.43	0.35	0.44	0.35	0.09	0.96	0.32	0.52	0.32	0.24	1.14	0.46	0.60	0.44	0.33	1.11	0.51	0.26	0.09	0.15	0.37	0.25	0.40	0.38	0.09	1.55	0.31
Benzo(a)anthracene	0.69	1.03	0.13	2.23	0.32	0.21	0.14	0.08	0.42	0.17	0.21	0.17	0.08	0.50	0.16	0.18	0.05	0.13	0.23	0.18	0.12	0.04	0.07	0.16	0.12	0.15	0.05	0.07	0.23	0.14
Chrysene	0.29	0.20	0.00	0.45	0.11	0.45	0.37	0.13	0.99	0.34	0.32	0.26	0.10	0.81	0.26	0.44	0.26	0.18	0.71	0.38	0.23	0.08	0.13	0.34	0.21	0.29	0.14	0.08	0.54	0.25
Benzo(b)fluoranthene	0.33	0.21	0.15	0.64	0.29	0.41	0.27	0.13	0.78	0.34	0.28	0.20	0.11	0.62	0.23	0.21	0.18	0.01	0.36	0.11	0.17	0.06	0.11	0.26	0.17	0.23	0.11	0.10	0.45	0.21
Benzo(k)fluoranthene	0.15	0.09	0.01	0.23	0.09**ab**	0.37	0.25	0.12	0.66	0.29**b**	0.16	0.06	0.09	0.26	**0.16ab**	0.15	0.15	0.01	0.31	**0.08ab**	0.11	0.04	0.08	0.18	**0.10a**	0.18	0.12	0.05	0.41	**0.15ab**
Benzo(e)pyrene	0.24	0.22	0.00	0.53	0.09**a**	0.35	0.24	0.09	0.60	0.26**b**	0.24	0.19	0.08	0.58	**0.19ab**	0.35	0.19	0.19	0.56	**0.32b**	0.76	1.53	0.00	3.50	**0.06a**	0.21	0.14	0.00	0.40	**0.11ab**
Benzo(a)pyrene	0.63	0.78	0.01	1.75	0.23	0.76	0.48	0.14	1.33	0.59	0.55	0.63	0.08	1.64	0.31	0.76	1.20	0.01	2.15	0.15	1.07	1.62	0.01	3.83	0.19	2.31	2.06	0.01	6.05	1.07
Indeno(1,2,3-cd)pyrene	0.16	0.10	0.01	0.21	0.09a	0.40	0.26	0.11	0.62	**0.30b**	0.29	0.26	0.11	0.80	**0.23a**	0.17	0.08	0.11	0.26	**0.16a**	0.11	0.04	0.06	0.16	**0.10a**	0.16	0.11	0.04	0.38	**0.13a**
Dibenz(a,h)anthracene	0.12	0.08	0.02	0.19	0.09	0.15	0.14	0.03	0.38	0.11	0.12	0.10	0.05	0.31	0.09	0.27	0.33	0.06	0.65	0.16	0.06	0.02	0.03	0.08	0.06	0.09	0.07	0.03	0.24	0.07
Benzo(ghi)perylene	0.27	0.16	0.04	0.42	0.20	0.46	0.30	0.13	0.80	0.36	0.24	0.17	0.07	0.56	0.19	0.40	0.23	0.21	0.65	0.36	0.18	0.07	0.12	0.28	0.17	0.31	0.29	0.05	1.06	0.23
Coronene	0.28	0.13	0.10	0.43	0.25	0.36	0.14	0.21	0.54	0.34	0.27	0.14	0.16	0.54	0.24	0.26	0.24	0.03	0.51	0.16	0.24	0.15	0.16	0.50	0.22	0.26	0.12	0.17	0.55	0.24
1,4-Naphthoquinone	0.47	0.36	0.05	0.86	0.30	0.53	0.31	0.25	0.92	0.46	0.27	0.03	0.25	0.33	0.27	0.31	0.06	0.25	0.35	0.31	0.30	0.07	0.25	0.43	0.30	0.38	0.23	0.22	0.87	0.34
2-methyl-1,4-naphthoquinone	1.13	0.59	0.54	1.78	1.01	1.04	0.68	0.53	1.89	0.88	0.55	0.02	0.53	0.59	0.55	0.62	0.10	0.53	0.74	0.62	0.62	0.18	0.53	0.95	0.61	0.81	0.52	0.48	1.94	0.70
Acenaphthenequinone	1.10	1.22	0.05	2.33	0.31	1.46	1.02	0.71	2.60	1.20	0.62	0.28	0.05	0.77	0.46	0.81	0.15	0.72	0.98	0.80	0.84	0.25	0.71	1.28	0.81	0.83	0.68	0.05	2.25	0.46
9,10 anthraquinone	2.34	2.22	0.13	5.05	1.21	3.23	3.56	0.81	8.99	1.97	0.80	0.07	0.75	0.94	0.80	1.01	0.40	0.75	1.47	0.96	2.00	2.43	0.77	6.34	1.33	1.21	0.75	0.69	2.82	1.06
2-methyl-anthraquinone	1.83	1.66	0.12	3.93	1.01	1.62	0.99	0.89	2.78	1.39	0.94	0.18	0.78	1.29	0.92	1.03	0.29	0.86	1.36	1.00	1.37	0.83	0.83	2.80	1.22	2.49	4.12	0.74	15.34	1.44
2,3-dimethyl-anthraquinone	1.41	1.11	0.06	2.51	0.73	1.49	0.99	0.75	2.69	1.24	0.79	0.03	0.76	0.83	0.79	0.86	0.15	0.77	1.03	0.85	0.89	0.28	0.76	1.38	0.86	1.16	0.74	0.69	2.78	1.00
Benz(a)anthracene 7,12-dione	2.60	3.14	0.18	7.15	1.25	1.43	0.90	0.67	2.62	1.22	0.76	0.08	0.69	0.91	0.76	0.81	0.13	0.73	0.96	0.80	0.83	0.25	0.66	1.26	0.80	1.04	0.63	0.61	2.40	0.91
5,12-naphthacene-quinone	0.09	0.00	0.09	0.09	0.09	3.35	4.97	0.09	11.93	0.84	1.96	3.42	0.09	8.79	0.46	0.40	0.53	0.09	1.01	0.20	0.36	0.41	0.09	1.01	0.20	0.54	0.79	0.09	2.47	0.22

ANOVA ($p < 0.05$) has been used to test for statistically different concentrations between transport modes. Numbers shown in bold were statistically different as indicated by the different letters associated with each. For the concentrations in normal font, there was no significant difference.

Moreover, PAHs and oxy-PAHs obtained concentration were higher than the reported for a rural area in Weybourney England (Alam et al., 2013a). Normally, PAHs and oxy-PAHs are predominantly emitted from vehicle motor emissions or fuel combustion (Wu et al., 2014, Li et al., 2015b). Therefore, PE concentrations were constituted by both sources of emission.

6.4.4.4 Home characteristics

The home concentrations were also analysed, the most used cooking fuel was electricity (N=21) followed by natural gas (N=13). The evaluation of home concentrations did not show a statistical difference between cooking fuel used for PAHs (Appendix 13). However, a higher concentration can be observed for compounds such naphthalene and phenanthrene, pyrene and benzo (a) pyrene. The wood combustion composition profile shows that the most abundant compounds are naphthalene and phenanthrene and this is similar to the obtained results in this study (Shen et al., 2012a, Shen et al., 2011). Pyrene is commonly emitted from petrol or diesel vehicles (Kliucininkas et al., 2011). Benzo(a)pyrene obtained concentrations for natural gas (0.55 ng m^{-3}) and electricity (0.37ng m^{-3}) were lower than the reported for wood cooking combustion (700 ng m^{-3}) and (290 ng m^{-3}) for LGP (liquid petrol gas) (Bhargava et al., 2004).

Oxy-PAHs like benzo (a) anthracene 7,12-dione concentration were found to be higher for natural gas fuel (independent t-test $p>0.05$). According to (Albinet et al., 2007), the dominant source of this compound is produced by diesel vehicle. 9,10 anthraquinone, typically emitted by diesel vehicles or generated by photochemical reactions, was observed to have a higher concentration in both fuels analysed (Albinet et al., 2007, Ringuet et al., 2012). High concentrations were also observed for 2-methyl-1,4-

naphthoquinone and 2-methyl-anthraquinone. These results suggest that indoor concentrations are more related to outdoor infiltration into the indoor more than produced at the indoors.

6.4.4.5 Type of occupation

Work concentrations were analysed based on the occupation of the subjects. No statistical difference was observed between the three occupation categories (one-way ANOVA $p>0.05$). However, higher concentrations for compounds such phenanthrene, anthracene, fluoranthene and chrysene were00 observed for students compared with office workers (Appendix 14). Most of the students were from University of Birmingham where offices faced the constructions activities that were developed inside the campus (Maertens et al., 2008, Soltani et al., 2015). Indoor PAHs in work environment might be attributable to the outdoor construction activities set in the university.

6.4.5 Possible contributors based on the percentiles

To estimate possible emission sources, 90th percentile values of PAHs and oxy-PAHs from PE concentrations were calculated. By using the 90th percentile, the concentrations were classified in 90th percentile + and 90th percentile – which correspond to concentration higher or equal to the 90th percentile and concentration below the 90th percentile (Appendix 15). Concentrations corresponding to individual subjects were correlated with the time activity diary using a Microsoft Windows Access database. According to the results, almost 60 % of the time when the concentrations were in the 90th percentile was spent in the home microenvironment, from which around 40 % of the time was when spend in the bedroom and this was observed in both percentiles. Obtained values are similar to the reported by (Gariazzo et al., 2015).

The major sources of contribution were considered based on the percentage difference, i.e., if the activity was only registered in the 90th + percentile or the percentage was higher in this section, the activity was considered as a high contributor. In general, higher percentage in the 90th percentile – and +, of most of the compounds were registered for places that most of the volunteers had to visit such home or office-school microenvironments (Gariazzo et al., 2015) (Table VI-10). Nevertheless, compounds differences were registered because other visited places and activities developed by volunteers (TAD-concentrations). For instance, compounds that showed high contribution (%) in the 90th + percentile at office microenvironments were fluoranthene, phenenahtrene, benzo (a) anthracene, chysene and coronene among PAHs, reported values that were similar to the obtained results (Wolkoff et al., 1993, Destaillats et al., 2008, Sangiorgi et al., 2013) and 2- methyl-1,4, napthoquinone, acenathenequinone and 2,4 dimethyl-anthraquinone among oxy-PAHs. The living room microenvironment also showed almost the same percentages across the compounds displayed, however, in the 90th + percentiles higher percentage were registered for compounds such acenphthalene, anthracene, fluoranthene, benzo(b) fluoranthene, benzo(k) fluoranthene, indeno (1,2,3 –cd)pyrene and dibenz(a,h)anthracene.

Moreover, the real differences between the 90th percentile – and + were observed for locations that differed across volunteers. For instance, the commute mode was identified as a high contribution activity in most of the cases, and in previous studies, PAH concentrations associated with traffic emissions have been reported to vary with traffic volume, emission and intensity (Kuo et al., 2003, Albinet et al., 2007, Kliucininkas et al., 2011, Alam et al., 2013b, Houston et al., 2013). Since traffic emissions are a

well-documented source of PAHs, we assume that most of the compounds were emitted by vehicles. Most abundant PAHs emitted from the traffic were benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(g,h,i) perylene (Kuo et al., 2003, Kliucininkas et al., 2011).

However, differences can be observed between commute transports in car, street (which includes walking and cycling) and bus compared with train. The compounds observed in the 90th percentile+ were almost the same for the former group of transport modes, and the primary differences were observed for bus, where compounds like benzo (a) anthrachene, benzo (e) pyrene, dibenz (a,h) anthracene and benzo(g,h,i) perylene were not displayed in the 90th percentil +. On the other hand, in case of train commuters, compounds observed in the 90th + percetil were very specific such fluorene, benzo (a) anthracene, indeno- (1,2,3-cd) pryrene and 2-metyl anthraquinone, acenaphthoquinone, 2,3-dimetylanthraquinone.

Other significant differences, based on the observed percentage, were registered in microenvironments such as restaurants and pubs. Both venues were considered as contributors since most of the compounds were registered in higher percentage in the 90th + percentile. According to the literature, higher concentrations of PAHs have been found in indoor environments where cooking activity is undertaken (Bhargava et al., 2004, Shen et al., 2012b). Four rings PAHs have been reported to be associated with cooking activities (phenanthrene, anthracene, fluoranthene and crysene (Kuo et al., 2003). Compounds like benzo (a) anthracene, benzo (b) fluoranthene and dibenz(a,h) anthracene were specific from pub microenvironment. From the reported carcinogenic compounds to be found in the cooking sites chrysene and benzo (a) pyrene were

reported in both (pub/restaurant), and dibenz (a,h) anthracene which was only displayed at pubs microenvironments.

Among other indoor environments, the most relevant microenvironment were shops and other indoors (bank, other house, etc.), as these were reported in the 90th + percentile, while places like shops, shopping centre, library, concentrations were only detected 90th- percentile. Other indoor microenvironments sources that might contribute to the concentration could be location as based on the information reported in the TAD, bank and GP were localized at traffic roads. The difference between shop and other indoors were only for compounds such fluoranthene and phenanthrene, which were detected in the 90th percentile + for shops but not for other indoor microenvironments.

Outdoor concentrations (park, garden, etc.) were high for benzo (e) pyrene, although other compounds were found to be lower than the 90th percentile, and were displayed in the 90th - percentile. These results suggest that indoor concentrations are normally higher than the ambient environment.

Table VI-10 Correlation between the subject's activities and the PAHs and oxy-PAHs 90th + percentile concentrations.

Locations	Naph	Ac	Ace	Fl	Ph	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	I[1,2,3-cd]P	D[a,h]A	B[ghi]P	Cor	1,4NQ	2,6DTBQ	2MNQ	AceQ	AQ	2MAQ	2,3DMAQ	7,12BaAQ	5,12NAQ
Home	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Living room	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Kitchen	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Office	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Lab	x	x			x	x			x		x	x	x	x	x	x	x		x		x			x	x		x
Common room	x	x	x			x			x		x	x	x	x	x	x	x	x	x		x	x	x	x	x		x
Other office	x				x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Street	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x		x	x	x	x	x	x	x	x
Car	x	x		x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x
Car park																					x	x			x		
Bus	x	x	x	x	x	x	x	x		x	x	x		x	x			x	x	x	x	x	x	x	x		
Bus stop										x				x				x	x	x	x	x	x		x		
Train							x		x						x						x	x			x		
Train station									x						x												
Restaurant		x	x	x	x	x	x	x		x			x	x				x	x	x	x	x	x	x	x	x	x
Pub	x		x	x	x		x	x	x	x	x			x		x		x			x	x			x	x	x
Shop	x			x	x		x	x	x	x	x	x		x	x	x	x	x		x	x	x	x	x	x	x	x
Gym			x			x			x			x	x		x												
Other indoor	x						x	x	x	x	x	x		x	x	x	x	x		x	x	x			x	x	x
Park						x																					
Garden								x					x											x		x	
Petrol station												x			x		x										
Other outdoor													x														

6.5 Conclusion

Considering that PM is the host of many pollutants it is priority to measure PM, for this reason $PM_{2.5}$ was measured to determine PAHs and oxy-PAHs at personal exposure home and work microenvironments. In addition online $PM_{2.5}$ personal exposure samples were collected. The $PM_{2.5}$ integrated filter was compared with MicroPEM^{TM} sensor and with Birmingham Tyburn ambient central site. A high correlation was observed between the integrated filters and the sensor, however, sensor concentrations were underestimated as they were lower than those obtained from the filter samples.

Sensor concentrations were corrected by using the linear equation, although good correlation was observed, higher values were reported by the sensor than those observed in the CS. The filter integrate samples showed poor correlation but higher than the CS

Although no significant differences were observed for corrected sensor and central site, the sensor data was now overestimated showing higher concentrations. Therefore, although Micro PEM is very useful tool to assess personal exposure, the instrument needs to be validated as in some cases it shows negative or zero values, which might influence the correlations. As observed by comparing the integrated filters with the central site, no correlation was observed confirming what previous studies had shown and supported the fact that central sites concentrations cannot be used to estimate exposure and health risk over specific population (Du et al., 2010, Buonanno et al., 2014, Choi and Spengler, 2014, Bekö et al., 2015, Li et al., 2015a)

Particle PAHs and oxy-PAHs show high concentrations for work microenvironment which can be associated with the construction period observed at the Birmingham

University, as most of the recruited subjects were from this school sector. For oxy-PAHs that have not been previously measured at the personal, home and work level, it was noted that, from this data there is a high degree of variability in oxy-PAH concentrations. While the overall exposure levels are low, they are significantly influenced by the ambient conditions and available sources.

The obtained oxy-PAHs were higher or similar than those reported by other authors for Birmingham outdoor samples, suggesting that indoor activities might emit primary or secondary oxy-PAHs. Therefore, the importance of having the PE and indoor oxy-PAHs values to determine more realistic exposure and risk.

Further investigation is required to fully understand the nature of exposure of oxy-PAHs in the general population considering a wide range of determinants. Such ventilation, temperature, location outdoor vs indoor.

CHAPTER VII. BC CORRECTION FACTOR

7.1 Introduction

7.1.1 Aethalometer

The Aethalometer™ developed by Magee Scientific Company is the most used instrument for measuring real-time optical absorbing black or elemental carbon particles. Automatic operation and portability allow the Aethalometer to be used in different locations and for a long period of time (Hansen et al., 2007).

MicroAeth™ Model AE51 is the pocket edition real-time monitor which incorporates the same Aethalometer® technology that has been used worldwide (AethLabs, 2012). The instrument can operate continuously for up to 24 hours enabling its use in a wide range of microenvironments. For example, in India, the instrument was used to measure black carbon (BC) concentrations inside auto-rickshaws semi enclosed and three-wheeled vehicles (Apte et al., 2011) whereas in Beijing, information on BC/EC was collected in different regions and for different types of buses (Wang et al., 2011a). The MicroAeth has also been used for estimation of vertical profiles of BC (Ferrero et al., 2011) and for personal exposure measurements (Dons et al., 2011, Rehman et al., 2011, Delgado-Saborit, 2012).

7.1.2 Principle of operation

The MicroAeth collects the air sample on a T60 (Teflon coated glass fibre) filter media (Hansen, 2005). A sensor measures the optical transmission through the filter ticket using a stabilized 880nm LED light source and photo dione detector. Since the gradual accumulation of particles on the filter contributes to the gradual increase in attenuation (Wickramasinghe et al., 2012, Hansen, 2005), the microAeth calculates BC concentration (μg m^{-3}) using the following formula (Eq. VII-1):

Eq. VII-1

$$BC\ (Aethalometer) = \frac{A * \Delta ATN}{\sigma \mathrm{ATN} * \mathrm{Q} * \Delta \mathrm{t}}$$

Where:

A= collecting spot area (1.67cm^2)

$\sigma \mathrm{ATN}$ = optical absorption cross section (specific attenuation) of BC (m^2 g^{-1})

ΔATN =change in attenuation during the time interval $\Delta \mathrm{t}\ (\mathrm{min})$

Q= volumetric flow rate (m^3 sec^{-1}),

Δt = sampling time (sec)

The attenuation (ATN) is defined by Eq. VII-2:

Eq. VII-2

$$ATN = ln\left(\frac{Io}{I}\right)$$

Where:

I_o =light intensity of the incoming light

I = light intensity after passing through the filter (Weingartner et al., 2003).

7.1.3 Aethalometer data correction

Data obtained from the microAethalometer needs to be corrected for a range of factors including noise, loading, and mass attenuation, and several formulas have been proposed to deal with these effects. In general, given the semi-continuous nature of measurements, there are short- term fluctuations in the data, that will produce noise (Hagler, 2011). Then with an increase in the loading on the filter ticket, BC data could be miscalculated. This occurs when the aerosol particles are embedded in the filter, causing a reduction of the shadowing effect (Weingartner et al., 2003, Ferrero et al., 2011, Wang et al., 2011b). On the other hand, ATN (attenuation) increases gradually as the particles accumulated in the filter, this occurs normally when samples are taken

at very high rates or when the BC concentration are very low. As a results, the ATN values can either remain the same or decrease, leading to BC miscalculation. And finally a correction done on a mass attenuation cross section of the black carbon, which varies according to the source of the carbon and also contain a scattering component; consequently the default values incorporated in instruments such as the aethalometer need to be corrected. However, this correction cannot be applied as it is used with independent data from which to derive a correction (Weingartner et al., 2003).

7.1.3.1 Noise correction (Hagler, 2011)

MicroAethalometer can produce noise when samples are collected with a high time frequency or when the BC concentration is low. This optical or electronic noise can produce low or no changes in the ATN values, and because the BC concentrations are calculated based on the ATN difference, BC may be underestimated, or reported as negative values (Weingartner et al., 2003, Ferrero et al., 2011, Hagler, 2011). The US EPA developed an algorithm for post-processing of the data which consists of conducting a time averaging variable to avoid the negative or extreme positive values (Hagler, 2011). Then, to obtain the BC concentration, ATN and the surface density loading of the filter are used (Hansen, 2005). The internal calculation takes into consideration the ATN increment at very high rates or for low BC concentrations. However, an error can occur when the ATN values do not change or when the change is marginal. This can lead to an optical or electronic noise, creating extreme low or high and even negative values (Hagler, 2011). This algorithm does not correct the loading effect, although it can be used alongside the loading formulae.

7.1.3.2 Loading corrections

Correction proposed by (Virkkula et al., 2005)

Virkkula et al.,(2005) proposed a correction factor which was originally derived for the formula used in the Particle Soot Absorption Photometer (PSAP) because the operating principle is the same as the Aethalometer.

The original formula for PSAP formula is (Eq. VII-3):

Eq. VII-3

$$\sigma_{abs}(\text{corrected}) = \left(K_0 + K_1 \ln\left(\frac{I}{I_0}\right)\right)\sigma_0 - S\sigma_{sp}$$

Where

K_0, K_1 and S = empirical derived constants

σ_0= non corrected absorption coefficient

σ_{sp}= particle scattering coefficient

Virkkula et al., (2007) assumed that the correction function of the PSAP is the same as in the Aeathalometer, as the ATN is given by the 100 *(-ln(I/I_0)), and therefore, the ATN value can be used in the formula.

However, since some Aethalometers do not have a nephelometer in use, the σ_{sp} value cannot be obtained and is assumed to be equal to zero. For the correction algorithms K_0= 1 and S= 0, the only constant that needs to be calculated at the end is the corrected absorption coefficient and the formula that they proposed is the following (Eq. VII-4):

Eq. VII-4

$$\sigma_{abs}(\text{corrected}) = (1 + K * ATN)\,\sigma_{abs}(\text{non corrected})$$

Therefore, the corrected BC concentration is calculated using the following equation (Eq. VII-5):

Eq. VII-5

$$\mathrm{BC\ (corrected)} = \frac{\sigma_{\mathrm{abs}}(\mathrm{corrected})}{\alpha_{abs}} = (1 + \mathrm{K} * \mathrm{ATN})\mathrm{BC}_0$$

Where

σ_{abs} = non-corrected absorption coefficient

α_{abs} = mass absorption cross section of BC

BC_0 = raw BC

Finally, Virkkula calculated the *K* value using the time of the last measured data for the filter in the spot *i* ($t_{i,last}$) and the time of the first measurement data for the next filter spot ($t_{i+1,first}$) (Eq. VII-6).

Eq. VII-6

$$Ki = \frac{\mathrm{BC}_0(t_{i+1,fisrt}) - BC_0(t_{i,last})}{ATN(t_{i,last}) * BC_0(t_{i,last}) - ATN(t_{i+1,first}) * \mathrm{BC}_0(t_{i+1,fisrt})}$$

K value, another empirically derived constant, has also been reported to vary according to the sampling location, season, aerosol composition and age (Hansen et al., 2007, Raju et al., 2011).

Several researchers have used the Virkkula formula to correct the BC data. Raju et al. (2011) used the formula for measurements taken using Aethalometer in India. Aethalometer was used in Rochester NY where Wang et al., (2011b) used the same formula to correct the loading effect, as well as Park et al., (2010) who concluded that the empirical correction algorithms reduces the variation in the BC concentration. Also,

a comparisons conducted between the original BC and corrected BC and EC concentration on 24-hours integrated filter samples found that the corrected BC data and the EC data were more comparable because of the correction for the loading effect. In fact, Collaud Coen et al. (2010) considered the Virkkula correction as a filter-loading correction instead of total correction of the attenuation coefficients in their evaluation of several correction algorithm since the authors did not include the multi scattering correction.

Correction proposed by (Apte et al., 2011)

The formula proposed by (Apte et al., 2011) is a modification of the original formula given by Kirchestetter and Novakov (2007) to calculate BC mass loading and attenuation coefficient. Since BC is the primary light absorbing aerosol species, the main objective was to prove that there is a strong indication that Aethalometer BC measurements are subject to the same source of error as measurements of absorption coefficient.

Kirchestetter and Novakov (2007) used an inverse diffusion flame as a BC source, which has two main characteristics: a nearly constant particles production rate and a BC particle production. As a result, they found that Aethalometer concentrations decreased linearly with decreasing filter transmission, and they used the following correction formula (Eq. VII-7):

Eq. VII-7

$$BC = \frac{BC_o}{0.60\ (0.88\ Tr + 0.12)} \propto \frac{ATN}{10(0.88\ Tr + 0.12)}$$

Where:

BC and BC_0 are the corrected and uncorrected BC concentrations,

Tr = measured filter transmission (Eq. VII-8) and

The constant 0.88 and 0.12 are the slope and the intercept of the regression line

Transmission is obtained by using the ATN measures:

Eq. VII-8

$$Tr = \exp\left(-\frac{ATN}{100}\right)$$

The Kirchestetter and Novakov (2007) formula was edited by Apte et al.,(2011) to be used to correct data from the microAeth AE51 (Eq. VII-9). The factor 0.60 was cut out from the formula as it was used by Kirchestetter and Novakov (2007) to adjust the difference between BC obtained from the Aethalometer and the thermal-optical analysis concentrations (Ban-Weiss et al., 2009). This formula has also been used by Wang et al.(2011a) to calculate BC concentrations from road emissions in Beijing and corrected the BC from the two wavelength Aethalometers (Model AE-21).

Eq. VII-9

$$BC = \frac{BC_o}{(0.88\,Tr + 0.12)}$$

To test the correction formula for the microAeth (AE51) data, Apte et al., (2011) made a cross-comparison measurements in which two AE51 ran together at the start of the sampling period.

7.1.3.3 Mass attenuation cross section

Weingartner et al., (2003) developed an empirical correction factor to convert the attenuation data into BC mass by adopting the absorption coefficient, which is defined

by the Lambert-Beer Law, and the attenuation coefficient (Eq. VII-10) (Ferrero et al., 2011).

Eq. VII-10

$$b_{ATN} \equiv \frac{A}{Q}\frac{\Delta ATN}{\Delta t}$$

Where

b_{ATN} = absorption coefficient

A =filter spot area ($7.1*10^{-6} m^2$)

Q =volumetric flow rate ($m^3\ s^{-1}$)

ΔATN= changes in attenuation during the time interval and

Δt = time interval (s)

The BC mass concentration is calculated by using the following formula (Eq. VII-11):

Eq. VII-11

$$M_{BC} = \frac{b_{abs}}{\sigma_{abs}} = \frac{b_{ATN}}{\sigma_{ATN} \bullet R(ATN)}$$

Where

b_{ATN}= aerosol absorption coefficient

σ_{ATN} = mass attenuation cross section ($12.55\ m^2\ g^{-1}$)

R(ATN)= aerosol loading factor

R=0.4+0.6 exp (-ATN/100 %)

7.2 Objectives

To compare the loading correction results by using two formulae and determine the most appropriate loading BC correction factor to be used on the FIXAT data.

To test the recently released USEPA noise correction algorithm on BC data to reduce the sampling fluctuations.

7.3 Methodology

7.3.1 Sampling methodology

BC data was collected using two MicroAeth instruments (AE51) and considered different sampling criteria as described in Table VII-1. Stationary samples were collected at an urban background site (Elms Road Observatory Site) in Birmingham UK and personal exposure samples were collected in Birmingham (UK). Two correction factors will be considered for this data, the noise and loading.

Table VII-1 BC sampling criteria and conditions

Conditions	Set 1	
Code	1.1	1.2
Device ID	1	2
ID code	618	622
Sampling characteristics	Different locations	
Flow (mlpm)	100	100
Time base (s)	60	60
Sampling site	EROS	PE
Collection day	Same day	

7.4 Results

7.4.1 Virkkula et al., (2007) Correction

The Virkkula loading correction formula does not modify the extreme or negative values as can be observed in Figure II-1. Once the ONA program was applied before applying the loading effect (Virkkula formulae) clearly, the extreme values were normalized and the negative values were corrected as observed in Figure VII-2. Therefore, it is important to use both corrections factors (noise and loading) as ONA program will correct extreme and negative values to make the data more smooth (Figure VII-3).

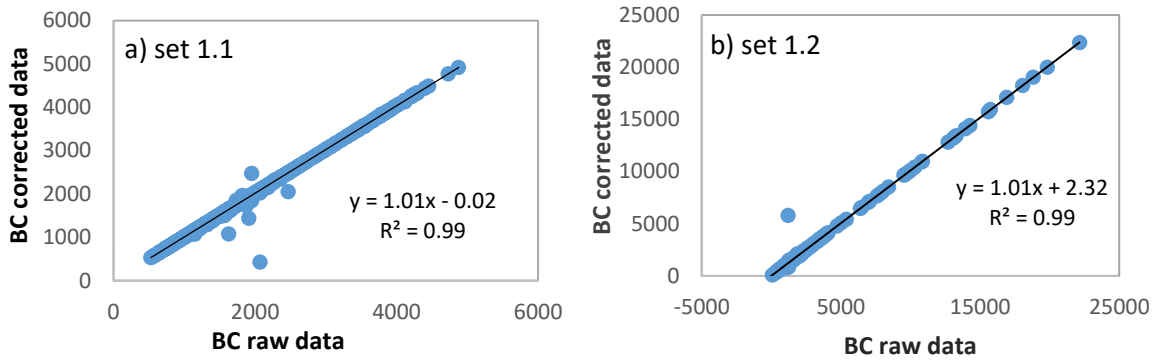


Figure VII-1 Correlation between raw and corrected BC using Virkkula formula (concentrations in ng m-3).

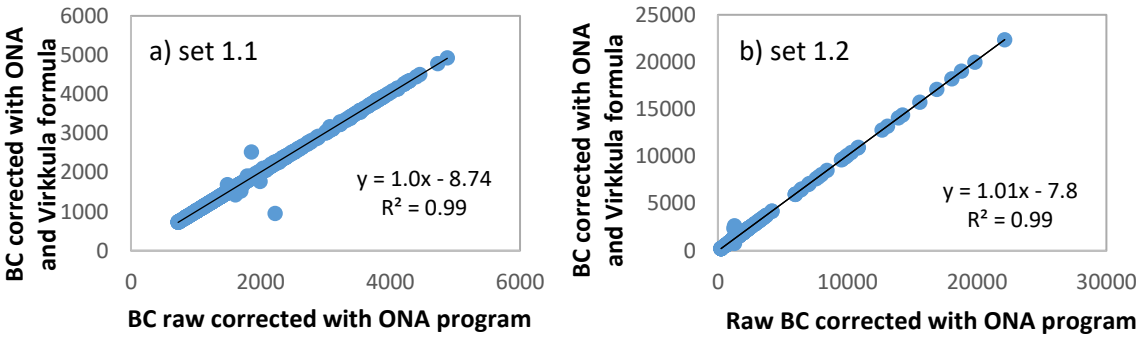


Figure VII-2 Correlation between Raw BC corrected with the ONA program and the Virkkula formula correction on the BC ONA correction (concentrations in ng m^{-3}).

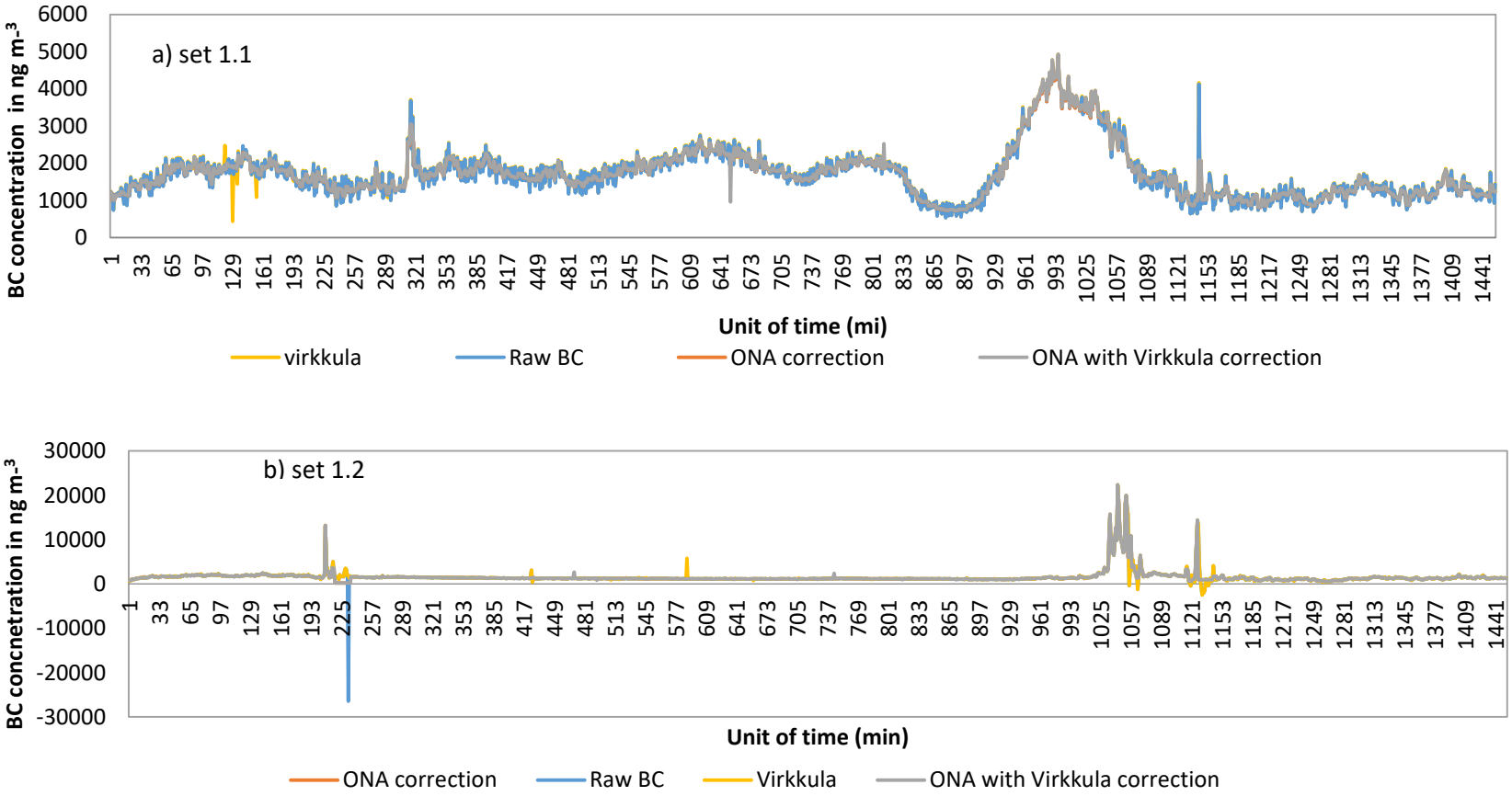


Figure VII-3 Comparison of the raw BC, BC corrected with Virkkula formula, the corrected with the ONA program and the corrected with ONA and the Virkkula formula.

7.4.2 (Apte et al., 2011) Correction

The Apte formula was applied to the MicroAeth measurements, and the correction removed the extreme values, as can be observed in Figure VII-4. However, similar to the previous correction, the negative values were not corrected just by using the formula.

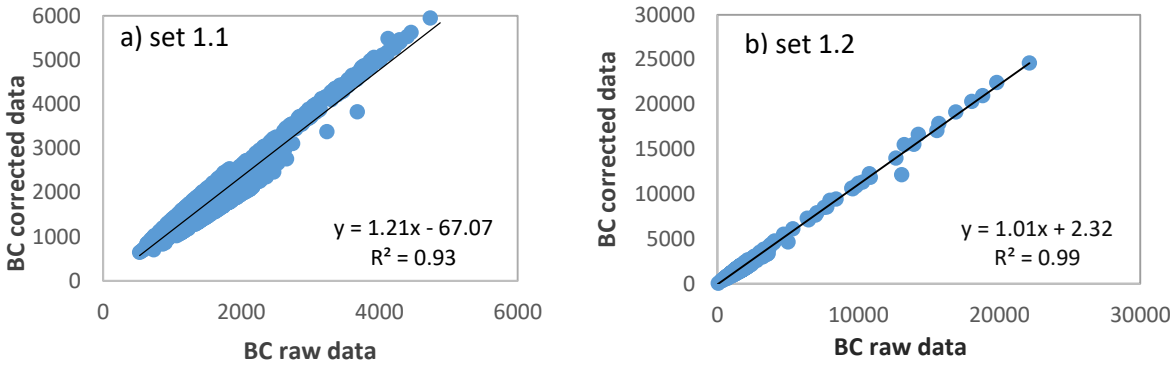


Figure VII-4 Correlation between raw and corrected BC measurements using the AE51-4 data (ng m^{-3}) and applying (Apte et al., 2011) formula.

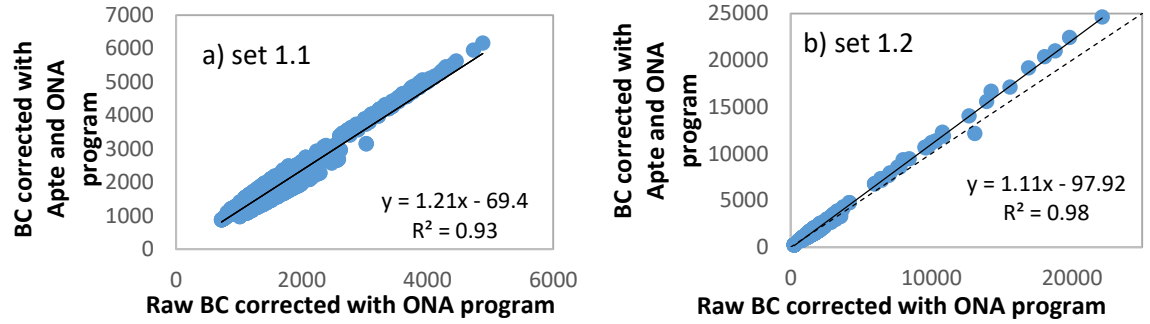


Figure VII-5. Correlation between raw (using the ONA program) and corrected BC measurements using Apte correction and ONA program (ng m^{-3}).

When the ONA noise correction program was used in the data, it was appreciable that no significant changes were reported for values that were originally positive (set 1.1) (Figure VII-5). However, the ONA program changed negative concentrations to positive, keeping the good correlation between the BC corrected with the ONA program and the BC corrected with ONA and Apte formula (set 1.2).

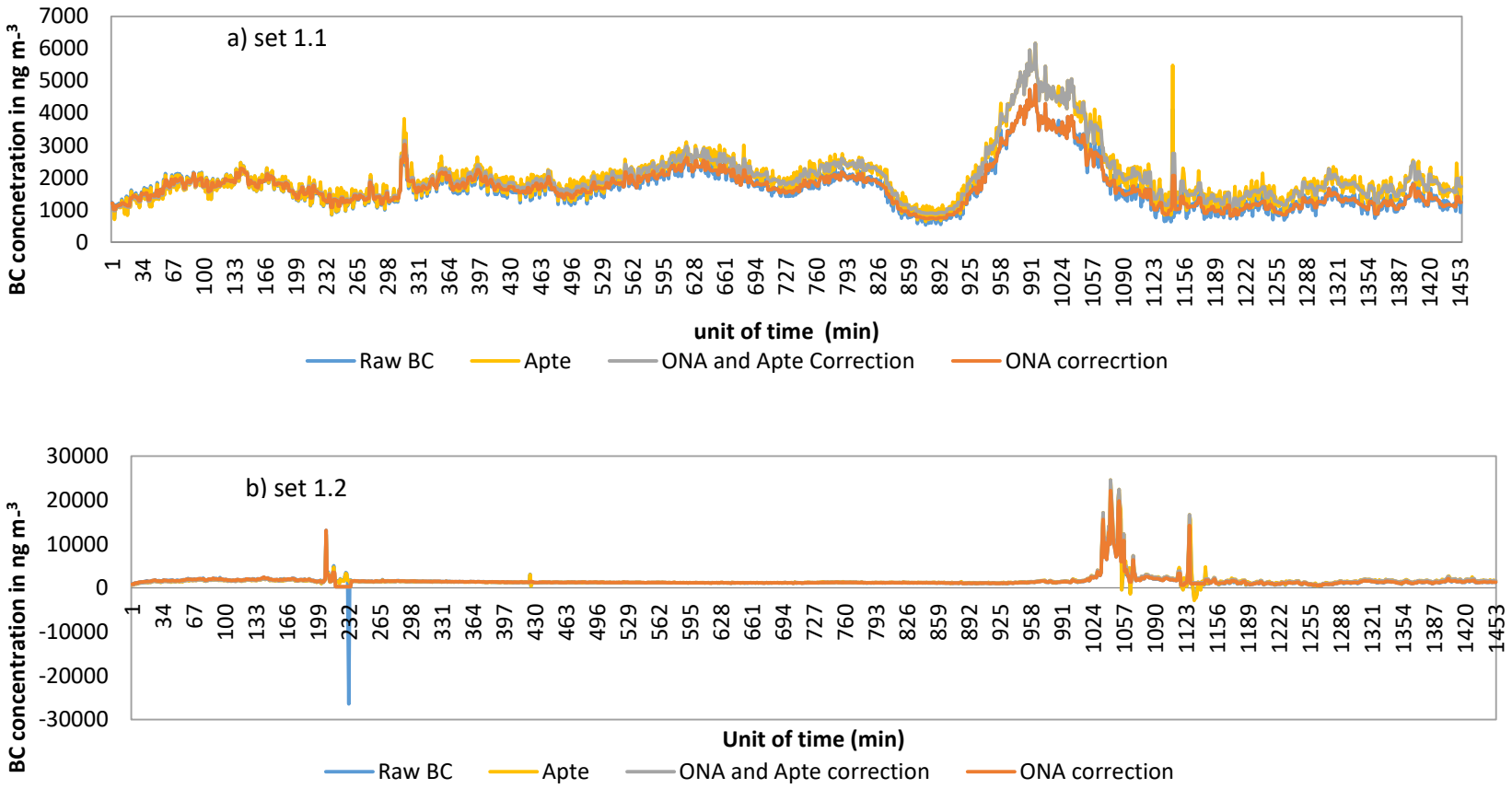


Figure VII-6 Raw BC, BC corrected with ONA program and BC corrected by using Apte formula and ONA program (ng m^{-3}).

The effect of the Apte formula on the BC raw data can be seen by plotting the raw BC against the ONA corrected and the ONA plus Apte correction (Figure VII-6). By using only the Apte formula, the extreme values were not corrected, while the ONA algorithm corrects the negative values as well as the extreme positive values. Notably, the combination of the loading formula and the noise correction brings the values to a medium term. This means that it is not too high with only Apte correction, and not too low as raw data.

7.4.3 Inter comparison of the BC correction formulas

The negative and extreme positive values registered during the sampling cannot be corrected by using the loading formulae (Virkkula and Apte). Therefore, the ONA algorithm needs to be used prior to loading effect to correct the underestimated BC concentrations.

In general, BC data treated for the noise and the loading effect by using Virkkula formula show a similar trend, as the BC concentrations corrected with ONA program (Figure VII-7). On the contrary, use of Apte formula on BC concentrations corrected for noise (ONA program) reflects an increase in the concentrations compared with BC noise corrected data. The loading effect can under-estimate the BC concentrations as the filter becomes darker (Apte et al., 2011, Ferrero et al., 2011, Weingartner et al., 2003), and the Apte formula corrects the miscalculations introduced by the loading effect.

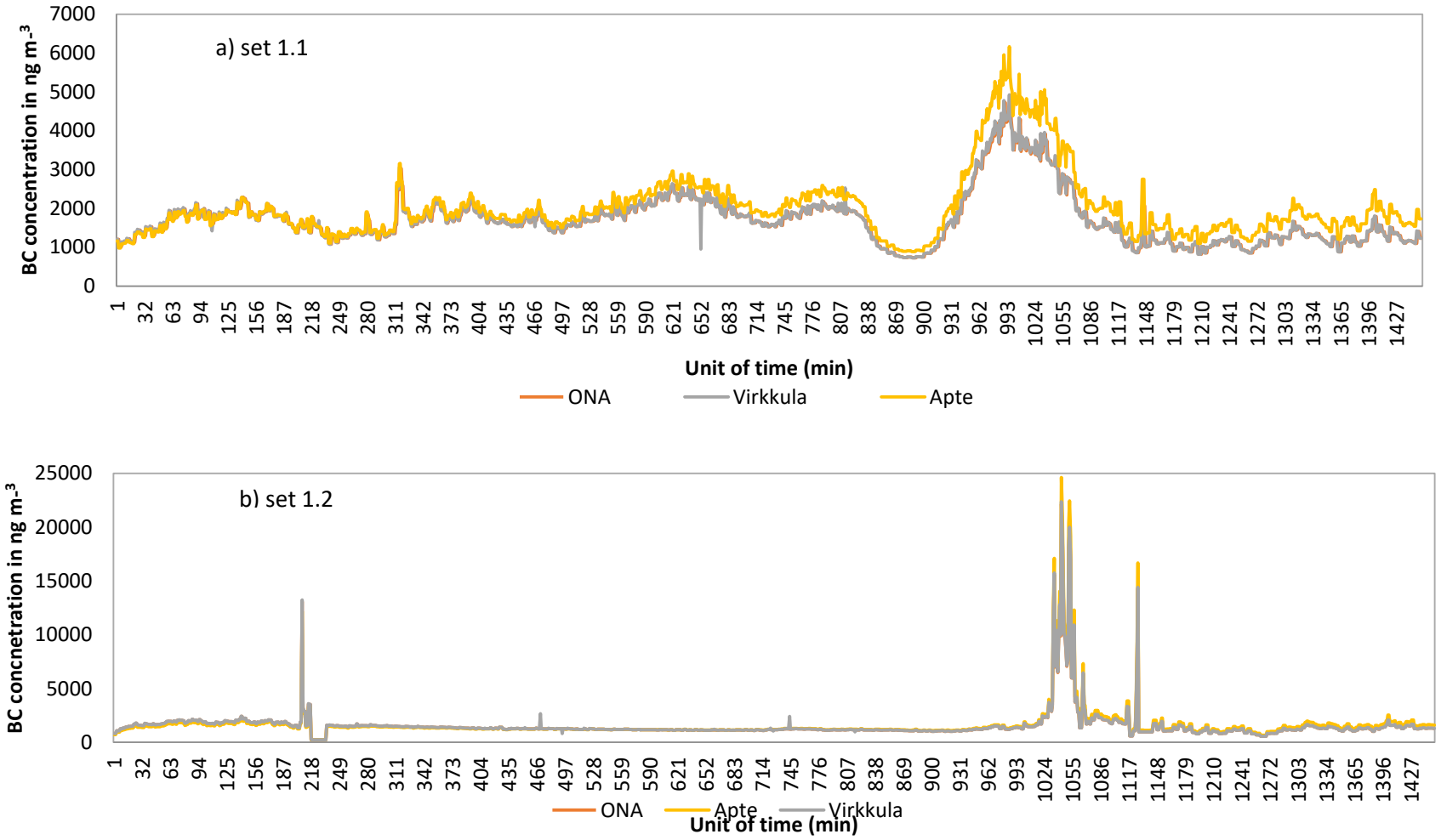


Figure VII-7 Apte and Virkkula correction formulas in the ONA corrected BC data with BC ONA corrected concentrations.

7.5 Conclusion

The loading correction factors and the noise correction algorithm were reviewed in this study, with the objective of selecting the most appropriate correction factors to be applied to FIXAT data. The Aethalometer typically underestimates BC concentrations when the mass loading on the filter is high, i.e. when samples are collected in high-concentration environments (Jimenez et al., 2007).

Application of the correction factor proposed by Virkkula suggests a positive correlation between corrected and non-corrected values, and the results appear to be stable across all the datasets. Apte formula has been used in previous studies to correct BC data from the MicroAeth and the effect of the formula over the data show a reduction of the extreme positive values and increment in the negative and low BC concentration obtained because of the darkness of the filter. Difference can be observed when Apte loading correction, noise correction and loading-noise correction were plot.

Based on the results of this study, we conclude that BC concentrations need to be treated for noise and loading effect. Correction produces more consistent concentrations and rids the dataset of extreme negative or positive data points. Apte formula corrected the under-estimated concentrations and therefore will be used to correct the BC data obtained from the personal exposure concentrations.

CHAPTER VIII. BC PERSONAL EXPOSURE

8.1 Introduction

BC is one of the major components of soot along with OC (Bice et al., 2009). BC is considered as highly light absorbing elemental carbon which size ranged mostly in the nucleation and accumulation mode (Hitzenberger and Tohno, 2001, EPA-US, 2010, Dotse et al., 2012, Huang et al., 2012b, Dons et al., 2013a, Ning et al., 2013). BC has a life time between 4-12 days which can vary between summer and winter (EPA-US, 2010, Cape et al., 2012). Combustion emissions including traffic and wood/biomass burning have been reported to be the most significant sources of BC (Dons et al., 2012, Delgado-Saborit, 2012, Dons et al., 2013a), and higher concentrations are typically observed during traffic hours during the morning and evening (Doumbia et al., 2012, Dons et al., 2012, Dons et al., 2013a). While temporal and local variations can affect observed BC concentration; the level of personal exposure is influenced by a range of factors including gender, activity pattern, age, physical fitness, and ambient BC concentrations (Jung et al., 2010, Lee et al., 2010, Raju et al., 2011, Jung et al., 2012, Li et al., 2015a). People typically spent most of their time in activities such work, commute, cook, rest, and take a shower. However, other activities such as going to the pub, restaurant, park, General practitioner, library, shopping centre, are often preformed less frequently, but may be associated with very high BC exposure. These activities have been considered to increase drastically the exposure to BC (Dons et al., 2011, Doumbia et al., 2012, Li et al., 2015a). Human health effects of BC exposure are not necessarily the same as those observed for PM (Janssen et al., 2011), and therefore, it is important to have a good understanding of BC emission and exposure

patterns in order to support epidemiological studies, as well as to create models to predict the exposure.

8.2 Objective

To characterize the BC concentrations considering the temporal and spatial variations.

8.3 Methodology

A MicroAeth^{TM} Model AE51 was used to collect air samples on a T60 (Teflon coated glass fibre) filter media at a fixed flow rate of 150 ml min^{-1}, with a time base of 300 sec (Hansen, 2005). A total of 30 subjects (15 from group two and 15 from group three) were recruited to participate, the recruitment, sampling criteria is described in (CHAPTER V). BC personal exposure samples were collected for 24 hours, subjects were asked to fill in questionnaires related to the places and activities developed during the sampling day, which were registered every time that subjects change activity or location. BC AE51 was only posted in the PE backpack, activities were tracked by using the TAD and the recorder

The MicroAeth normally runs for slightly less than 24 hours, therefore to avoid missing data, volunteers were asked to charge it during the night.

The BC concentration was downloaded into a database using the MicroAeth COM PC software. The post processing methodology recommended by Hagler et al., 2011 (US-EPA ONA algorithm) was used to correct data for noise and the formula proposed by Apte et al.,(2011) was applied to correct for the light scattering. Statistical analysis was conducted using SPSS 21 and Microsoft Excel 2013. TAD data was used to determine the relationship between BC concentration and the locations visited by the subjects and activities performed in each micro-environment.

8.3.1 Time- weighted contribution

To calculate the time-weighted contribution of various microenvironments to overall personal exposure to BC, the model proposed by (Harrison et al., 2009) was used (Eq. VIII-1). This consists of multiplication of the concentration of each microenvironment with the fraction of time spent in that microenvironment then dividing this with the total time spent in all microenvironments by the subject (% of contribution).

Eq. VIII-1

$$K = \frac{\sum_{i=1}^{I} \frac{t_{ik} \times X_{ik}}{T_i}}{\sum_{\mathrm{i=1}}^{\mathrm{k}} \sum_{i=1}^{I} \frac{t_{ik} \times X_{ik}}{T_i}} \times 100$$

Where t_{ik} is the time spent in a microenvironment *k* by subject *i*, X_{ik} is the average concentration of microenvironment *k* for subject *i,* and T_i is the total time spent in all microenvironments by subject *i*.

8.4 Results

8.4.1 BC activity-concentration and contribution

For this study, 30 volunteers participated and around 70% of the subjects were sampled twice, registering a total of 12329- 5 min observations. Activities from the TAD were categorized in five groups including home, work, in-transit, other indoors and outdoors activities (Table VIII-1). Data showed a positive skewed distribution, however the data was discussed considering the GM data. Average individual exposure concentration was 1481 ng m^{-3} values, and was similar to the BC concentration (1300 ng m^{-3}) obtained by (Delgado-Saborit, 2012) which sampling conditions were personal exposure measured to subjects who were student or office workers from the university of Birmingham UK .

The lowest average exposure (24 hours) for a subject was 302 ng m^{-3}. This subject spent most of the time at home and used the microwave to heat food, kept the windows closed and mainly worked on the computer. On the contrary, the highest average exposure concentration was (4110 ng m^{-3}) where the subject spent a lot of time outdoors and visited a pub and other indoor microenvironments. In general, across all subjects and microenvironments, the highest average BC concentration was obtained during commute (2753 ng m^{-3}) followed by other indoor and outdoor concentrations (1912 and 1928 ng m^{-3} respectively). In light of the fact that the primary source of BC is combustion, our results are in agreement with previous findings that report higher concentration during transport commute (Apte et al., 2011, Dons et al., 2011, Dotse et al., 2012, Dons et al., 2012, Buonanno et al., 2013b). The lowest average concentrations were registered while subjects spent time at work (1292 ng m^{-3}) and home (1056 ng m^{-3}). Concentrations were close to the results obtained by (Dons et al., 2012) of 1077 and 1360 ng m^{-3} for work and home respectively.

Table VIII-1 Summary of BC (ng m^{-3}) concentrations across various microenvironments (N= 5-min observation).

Microenvironment	N	Mean	SD	Min	Max	GM
Home	8242	1742	2113	32	34454	1056
Work	2677	1695	2125	136	47405	1290
Other indoor	552	6960	30941	136	359287	1912
In-transit	788	5652	9309	120	103960	2753
Outdoor	70	3152	4552	600	28048	1928

The commute concentrations were higher for volunteers using the bus (GM=7902 ng m^{-3}) (Table VIII-2) and the exposure concentrations for bus were similar to reported results in the literature - 6575 ng m^{-3} (Dons et al., 2012), 3800 ng m^{-3} (Buonanno et al.,

2013b) and 3500 ng m^{-3} (Delgado-Saborit, 2012). Car concentrations (4129 ng m^{-3}) were higher than those reported for Lexington, KY (2200 ng m^{-3}) (Lee et al., 2010) and Birmingham UK (2800 ng m^{-3}) (Delgado-Saborit, 2012), but significantly lower than values obtained for India (42000 ng m^{-3}) (Apte et al., 2011), for Belgium 6432 ng m^{-3} (Dons et al., 2012) and for Italy 6445 ng m^{-3} (Buonanno et al., 2013b). On the other hand, train concentration were similar to the observed at the train station 2824 and 2838 ng m^{-3} respectively, and values was similar to the reported by (Dons et al., 2012) for Belgium with 2394 ng m^{-3}. However, the BC concentrations in this study were lower than the reported by (Delgado-Saborit, 2012) of 5600 ng m^{-3}.

Observed concentrations can be influenced by the wind speed, traffic (Dons et al., 2013a, Gramsch et al., 2013), time of the journey (Dons et al., 2011, Lee et al., 2010, Li et al., 2015a), routes (Apte et al., 2011), and the air conditioning system among others. For instance, (Lee et al., 2010) reported that in-vehicle BC and $PM_{2.5}$ concentrations were higher during the morning and in the working day.

Other indoor microenvironment concentrations were also high, primarily locations visited were GP visits, pubs, shopping centres, shops, and gym, reporting BC level of GM=6034, 6736, 4028, 3241 and 3276 ng m^{-3} respectively. Shopping centre concentrations in this study were higher than the reported for Belgium with 2584 ng m^{-3} (Dons et al., 2011).

Although the exposure time in some of the microenvironments such as the library, nursery, other indoors, and supermarket(s) was short, concentrations ranged between 1500 to 2500 ng m^{-3}. Considering for instance GP concentrations which were almost similar to the bus, it is important to confirm the high values by testing acute exposure

during the daily activities. Despite the low time spent at the petrol station, subjects were exposed to BC concentrations higher than 10000 ng m^{-3} in a 15 min average time exposure. Sources of exposure were mainly the vehicular emissions from several vehicles. While subjects were at home, the exposure to BC (1056 ng m^{-3}) was lower and values were similar to the reported for Belgium (1223 ng m^{-3}) (Dons et al., 2011) and Birmingham, UK (950 ng m^{-3}) (Delgado-Saborit, 2012), but lower than concentrations reported for Ghana -14500 ng m^{-3} (Van Vliet et al., 2013).

However, noticeably high BC concentrations were observed in kitchen microenvironment (2175 ng m^{-3}), which can be attributable to the location of the microenvironments (kitchen room was between the living room and the bathroom). Previous kitchen measurements reported concentration of 1600 ng m^{-3} (Delgado-Saborit, 2012).

Considering no only the location but also the activities developed higher exposure can be observed for subjects traveling by bus (8115 ng m^{-3}) more than just waiting at the bus stop (1499 ng m^{-3}). A lower concentration was observed for cycling (2187 ng m^{-3}) and walking (2236 ng m^{-3}), these obtained values were similar to the previous study developed in Birmingham, UK with 1300 and 3200 ng m^{-3} respectively (Delgado-Saborit, 2012) and lower than the reported values for Belgium with 3175 and 3555 ng m^{-3} respectively (Dons et al., 2012). And for Xuhui District, Shanghai which reported BC concentration of 6580 and 5590 ng m^{-3} respectively (Li et al., 2015a). Subjects reported to be sitting outside such as in parks, garden, or in front of the house registered an average concentration of 3058 ng m^{-3}.

Table VIII-2 BC concentrations in ng m^{-3} grouped by visited places (N=5-min).

Location	N	Mean	SD	Min	Max	GM
Bus	64	11825	13872	1481	72283	7902
Bus stop	9	1562	489	985	2580	1501
Car park	13	431	60	313	518	428
Car	158	7958	12336	120	103960	4129
Nursery	2	1616	733	1098	2135	1531
Garden	20	1586	741	600	3414	1411
GP	10	6572	2568	2484	9934	6034
GYM	104	4335	3491	995	12972	3276
Home	687	2361	2397	283	21043	1610
Bathroom	77	2550	3241	383	24445	1688
Bedroom	5525	1312	1454	33	16871	827
Kitchen	541	3100	2889	126	25295	2178
Living room	1412	2561	2989	144	34454	1660
Lab	234	1002	540	136	3082	878
Library	15	2187	982	1045	5380	2038
Other indoor	27	3857	3322	560	11367	2434
Other outdoor	30	2644	5125	711	28049	1466
Park	5	3110	1684	1725	5266	2772
Petrol station	3	16538	2163	14739	18939	16447
Pub	53	46042	90854	923	359288	6736
Restaurant	50	5662	9467	459	48744	2814
Shopping centre	2	4226	1810	2946	5506	4028
Shops	34	4326	4863	565	29218	3241
Street	493	3995	5883	259	67355	2241
Supermarket	21	3416	3122	259	13669	2127
Train	46	8912	14029	377	54808	2824
Train station	17	5020	6891	558	24893	2838
Common room	227	1367	797	136	4560	1150
Other office	96	2323	2129	454	14176	1830
Office	2354	1701	2206	144	47405	1286

Home activities that provide higher concentration were; household activities like DIY, tidying, cleaning, dusting, vacuuming and other activities at home which involve movement (Table VIII-3). It is documented that kitchen activities such cooking, baking, and frying contribute to the high concentrations in this microenvironment (Custódio et al., 2014). Our results are in agreement since the obtained concentration for frying were 2748 ng m^{-3}, followed by cooking/baking 2053 ng m^{-3}.

High BC average concentrations can be observed while subjects socialize (6918 ng m^{-3}). The obtained values are higher than the report for previous studies 1525 ng m^{-3}

(Dons et al., 2011). The lowest concentrations were observed while subject slept (785 ng m^{-3}) and the values are in agreement with those obtained by (Dons et al., 2011) with 1153 ng m^{-3}.

Table VIII-3 Statistics from the BC concentrations in ng m^{-3} grouped by volunteer activities (N=5-min).

Activity	N	Mean	SD	Min	Max	GM
Travelling on bus	63	11990	13921	1538	72283	8115
Waiting at bus stop	10	1554	461	985	2580	1499
Driving a car	165	7592	12191	120	103960	3575
Sat in the car at the car park	6	1718	661	822	2362	1591
DIY	25	4743	520	3965	5954	4715
Cooking/ baking	401	3048	2879	126	22617	2053
Frying	10	5077	7408	789	25295	2748
Preparing food	27	3105	1704	1208	7618	2683
Beauty treatment	2	1146	46	1113	1179	1145
Cleaning /dusting	101	3335	2305	1135	15149	2777
Tidying/vacuuming	22	3262	1695	1411	7271	2872
Indoor activities-home	370	2400	2384	251	24445	1694
Indoor activities other	19	4204	3197	968	11367	3120
Outdoor activities	30	1107	436	600	2406	1038
Re-fulling car	3	16539	2163	14739	18939	16447
Socializing/visiting	38	46481	100710	1679	359288	6918
Travelling on train	46	8912	14029	377	54808	2824
Waiting at station	14	5656	7478	558	24893	3057
Working inside	2430	1722	2197	144	47405	1304
Working in lab	234	1003	540	136	3082	878
Sleeping	4792	1264	1453	33	16871	785
Walking	451	4062	6074	259	67355	2236
Shopping	48	3914	4474	259	29218	2636
Cycling	35	3286	3392	502	15273	2187
Sitting outside	24	3497	1905	1124	8776	3058
Other sport	30	2645	5125	711	28049	1466
Computer/paperwork	719	1374	1161	210	12692	1005
Indoor activities with movement	132	3738	3365	454	12972	2599
Relaxing/reading/eating	2076	2860	6998	47	172653	1678

8.4.2 BC considering home characteristics

BC home base activities were selected from the pool of concentrations data to be compared with the type of fuel used by FIXAT subject. Higher concentration were observed for subjects using gas as cooking fuel 2046 ng m^{-3} compared with electricity

1434 ng m^{-3} (independent t-test p>0.05) (Table VIII-4). These differences were also reported during a study developed in Birmingham UK (Delgado-Saborit, 2012).

Table VIII-4 BC concentration considering the two most used cooking fuels (ng m^{-3}) (N=5-min).

Cooking fuel	N	Mean	SD	Min	Max	GM
Electricity	4086	1434	1839	57	34454	910a
Gas	4156	2046	2312	32	24444	1222b

Independent t-test show significant mean differences at the 0.05 level (expressed by different letter).

Home concentrations were also compared with the volunteer's house location, based on the results observed in Table VIII-5. Higher BC concentration was registered for houses localized in the sub-urban area (1772 ng m^{-3}), and this was statistically different from the mean concentration reported for the rural areas (1251 ng m^{-3}) based on ANOVA analysis. The city centre reported to have the highest GM which suggests that the high maximum concentrations observed in the sub-urban area may well have influenced the arithmetic mean.

Average BC concentration on traffic roads (4800 ng m^{-3}) was almost double the concentration than low traffic roads (2700 ng m^{-3}) (Delgado-Saborit, 2012). Urban, suburban and urban reported BC average concentration was 2138, 1160 and 1367 respectively for Belgian houses (Dons et al., 2011).

Table VIII-5 BC concentrations considering the house location (ng m^{-3}) (N=5-min).

House location	N	Mean	SD	Min	Max	GM
Rural area	316	1251	1052	141	7271	817a
Sub-urban	7589	1772	2178	32	34454	1062b
City centre	337	1534	1020	248	4999	1170 ab

ANOVA test using harmonic mean and type III error for the differences in number of samples per group. Mean differences are expressed by different letters.

8.4.3 BC time–weighted contribution

To determine the influence of the time over the average concentration the time-average percentage was calculated by using the formula given in Eq. VIII-1. The results show for instance that even though the exposure at home was for a longer period of time the contribution of this microenvironments were relatively lower (Table VIII-4). On the other hand, for in-transit activities the opposite trend was observed despite lower exposure duration, the time-weighted contribution was higher due to the higher concentration. The effect of time- weighted percentage was observed for other indoors and work activities. For indoors the time- weight contribution percentage was higher than the time exposure percentage and it was caused by the high concentration observed for those microenvironments.

Although the highest concentrations were registered by other indoor microenvironments (Table VIII-1), their contribution to total personal exposure was minimal (Figure VIII-1). However, we cannot ignore the high concentrations just because limited time is spent in these environments.

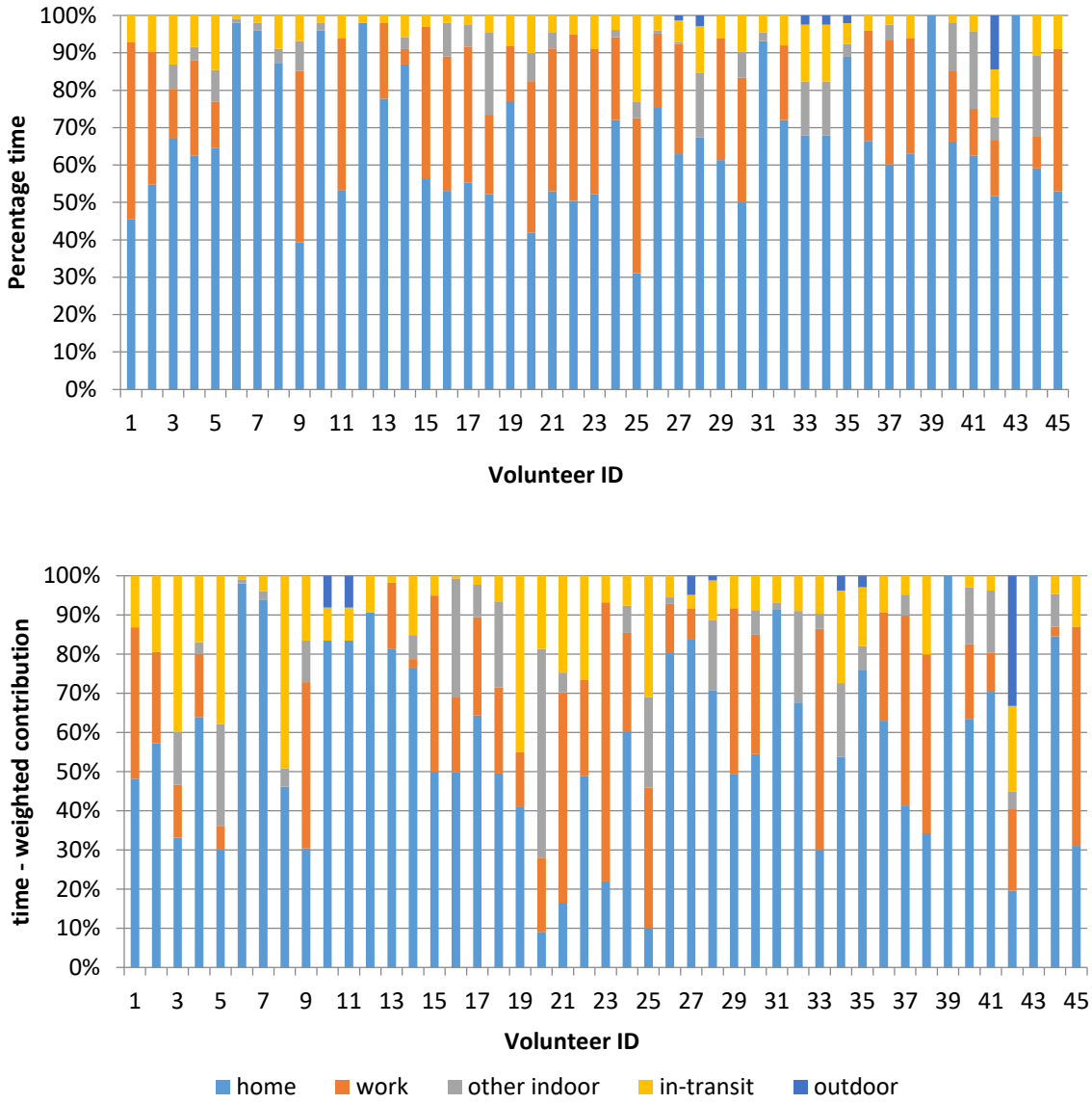


Figure VIII-1 BC microenvironment time-exposure and time- weighted percentage.

8.5 Conclusion

Volunteers recruited for this study were mostly students or office workers, and most of them lived in semi-detached houses. Results obtained in this study show the importance of considering personal exposure as the major approximation of the real exposure to a wide range of air pollutants. It has been reported that a higher

concentration will be found during the personal exposure than the one obtained for specific microenvironment and form ambient samples.

On average, subjects had a daily exposure of 1481 ng m^{-3}, but acute exposure was observed while subjects visited the petrol station(s) registering an average 15min exposure of 16447 ng m^{-3}. The highest contributor to the exposure were vehicle emissions (bus and car) and cooking emissions (home and pubs kitchen) with a low percentage of exposure time, but higher time weighted contribution percentage.

To develop models to predict the BC exposure, it is not only necessary to have personal exposure readings considering different ambient conditions, but also to cover a wide range of microenvironments. According to the literature and because these are the activities that had been most studied, it is known the high amount of BC emissions occur during the commute mode. However, based on the findings, other microenvironments can also contribute to the high exposure. Therefore, in addition to the normal activities (e.g. cooking, commute, rest, work), we should look at those subjects that will work as outliners to avoid underestimated exposure.

Epidemiological studies need to be developed to determine the real effect of BC on human health and studies can be enriched by having a most complete exposure data. Therefore, it is important to continue collecting not only BC exposure data but also incorporate other variables such as health, genetic make-up, occupation and age seasonal variations, socioeconomic characteristics etc.

CHAPTER IX. EC, BC, BS DETERMINATION FROM TEFLON FILTER

9.1 Introduction

In recent decades, black carbon (BC) has been an important pollutant to investigate as it is primarily emitted by combustion. Moreover, it plays an important role in climate change as after CO_2 it can impact the amount of radiation absorbed (Jacobson, 2001, Baron Robert et al., 2011). BC has been recognized as a precursor of adverse health effect in the short and long term according to the World Health Organization (WHO). In addition, it has been reported that the health effects of BC might be greater than PM_{10} and $PM_{2.5}$ (Janssen Nicole A.H et al., 2011, WHO, 2012). The related health outcomes reported are airway inflammation in asthmatic adults, decrease of the cognitive functions in children, and positive correlation between BC and blood pressure (Suglia et al., 2008b, Wilker et al., 2010, Janssen et al., 2012).

BC has been defined as

> *"Carbonaceous aerosol that have strong light absorption across a wide spectrum of visible wavelengths (Hansen et al., 1984)".*

Black smoke (**BS**) has been defined as

> *"The carbonaceous fraction of the $PM_{2.5}$ originated from the combustion sources (Lai et al., 2006)".*

Elemental carbon **(EC)** is defined as

> *"Chemical term attribute to the thermal refractory carbon which is pure and not graphite (Chow et al., 2009)".*

Soot is considered as

> *"Black powder composed mainly from carbon, by-product of fossil and biomass combustion (Long et al., 2011)".*

Although the terms of BC, BS, EC and soot are commonly used as synonyms the original meaning suggests a difference such as thermal, optical and chemical properties (Lavanchy et al., 1999, Cyrys et al., 2003, Bond and Bergstrom, 2006, Bice et al., 2009, Quincey et al., 2009). Researchers suggest that the difference between BC, BS and EC is based on the measurement method and light absorption properties, as high correlation has been found between EC and BC and data from BS and BC instruments can be comparable with a positive correlation (Lavanchy et al., 1999, Streets et al., 2001, Adams et al., 2002, Quincey, 2007, Quincey et al., 2011, Long et al., 2013).

Particulate matter (PM) is important not only for the mass concentration but also for the size distribution and composition of the particles. One of the primary components of PM is the BC (Harrison et al., 2000, Quincey et al., 2009, Cahill et al., 2011). PM particle size fractions have been well investigated, in order to have a complete panorama of the health effects that PM might causes in the human health; it is indispensable to have the particle size fraction not only from the PM but also from the PM components. Although there are several instruments and models to calculate particulate matter size distribution such the Optical Particle Counter (OPC) (Gorner et al., 2012), Condensation Particle Counter (CPC) (Morawska et al., 2003), Scan Mobility Particle Sizer (SPMS) (Costabile et al., 2009, Padró-Martínez et al., 2012, Shi et al., 1999), Multi-Compartment and Size-Resolved Indoor Aerosol Model (MC-SIAM)

(Hussein et al., 2006), Mobile Platform (MP) (Kozawa et al., 2012), Micro-Orifice Uniform Deposit Impactor (MOUDI) (Ringuet et al., 2012), Portable Dust Monitors (PDM) (Géhin et al., 2008), no instrument is capable to give BC size fraction information directly. However recently, Ning et al.,(2013) reported the BC size fraction by using the differential mobility analyzer together with the MicroAethalometer AE51. Nevertheless to reproduce this study, several modifications needed to be done in the power voltage and flow rate of the Aethalometer. Moteki and Kondo (2010) determined the particle size distribution through laser-induced incandescence. Reddington et al.,(2013) used the data from the SP2 (Single Particle soot Photometer) and applied a model created to determine the BC size fraction distribution. Hitzenberger and Tohno (2001) had previously used the 10 stage impactor to finally analyse the samples by using the integrated sphere technique (IS); suspended BC particles are analyzed in the IS by irradiating them with an halogen lamp. There is a reduction in the light flux when the sample has absorbing substances. Then the signal reduction is converted to BC concentration by using a grade suspension of carbon black in 80 % of water and 20 % of isopropanol.

An indirect proposal to measure BC particle size distribution could be done by using the MOUDI. But this instrument uses a PTFE filter to collect the particles and this filter cannot be used in the Sunset Lab EC-OC analyzer to measure EC, as the instrument requires quartz-fiber filters. It can neither be used directly in the Smoke Stain Reflectometer (SSR) because, according to Loader (1999) the samples must be collected on Whatman grade 1 filter paper. Previous studies have determined the reflectance of the PTFE filters by using the SSR (Adams et al., 2002, Cyrys et al., 2003). However, the BS concentration could not be calculated, since the equation is

defined specifically for filter paper. Other studies have reported the absorption coefficient (absorbance), in both PTFE filter and filter paper using measurements of the SSR. However, the mass was not calculated (Cyrys et al., 2003, Quincey, 2007, Minguillón et al., 2012).

9.2 Objectives

The main objective of this study was to obtain the relationship between reflectance and BS data measured in the SSR from the Teflon filters with EC (measured in the EC/OC from quartz filters) and BC (measured with the MicroAethalometer AE51). In order to determine EC and BC particle size distribution from the Teflon filters used in the MOUDI to characterize EC or BC particle size distribution.

9.3 Methodology

The first relationship to investigate, was reflectance in the Teflon filter measured in the SSR with the BS calculated from the filter paper by using reflectance measured with the SSR and with the BS formula using proposed formulas from Loader,(1999) Minguillón et al.,(2012) and Quincey (2007). Secondly, real-time BC data was obtained from the MicroAethalometer and the relationship between BC and BS in the filter paper and Teflon filter reflectance and absorbance was investigated.

The final comparison was the relationship between reflectance measured in the Teflon filter; BS measured in the paper filter and BC measured in the MicroAethalometer with EC data collected in a quartz filter. The correlation between EC and BC has been well documented (Liousse et al., 1993, Hitzenberger et al., 1999, Lavanchy et al., 1999, Watson et al., 2005, Quincey et al., 2009).

9.3.1 Sampling

In this study an inter-comparison between different sampling filter media and instruments analysis was conducted. The samples were collected in Birmingham and London UK during the summer of 2013. The sampling sites were the Bristol road observatory site (BROS) -characterized to be near a heavy traffic road; and at Elms road observatory site (EROS) which is classified as an urban background site. The samples were collected for a period of 48 hours to ensure a reasonable filter loading. A second set of filters were taken at the sampling sites of the UK Air Monitoring Sampling Sites of the DEFRA Department. The selected sites were:

- Tyburn, considered as urban background sampling site in Birmingham, which is located roughly 600 meter to the north of the M6 motorway;
- Harwell, classified as a rural background neighboring by agriculture fields; North Kensington, characterized to be an urban background in London which primarily surrounded by residential buildings;
- Marylebone road, which is considered as the principal road to go in and out of the central London considered as an urban traffic site (DEFRA 2013).

The sampling period on the UK air sampling sites was 7 days. The sites were selected based on the well-known data reported that the primary source of EC, BC or BS is the vehicle exhaust emission (Keuken et al., 2012, Adams et al., 2002, Gianini et al., 2013).

PM was collected simultaneously on 47 mm Teflon (Membrane filter LCR hydrophilised, 0.5 µm pore size), quartz (Whatman QMA) and paper (Whatman No.1) filters. Filters were mounted on a filter holder and using an extraction pump capable to provide more than 18 L min^{-1}, as each filter was set to run with a flow rate of 6 L min^{-1}. Additionally, the MicroAethalometer (MicroAeth^{TM} Model AE51) was set for the same

sampling period in each of the sampling sites. The operation conditions were established at interval of 1-sec and 150 ml min^{-1}. After sampling the filters were wrapped in aluminum foil paper and stored in the freezer until analysis. A total of 30 samples were collected during the sampling campaign. The Teflon and filter paper were used to calculate the reflectance following the instructions proposed by Loader, (1999) the filters were measured using the digital SSR model 43D and the values were given in a percentage of transmitted light.

9.3.2 Analysis

9.3.2.1 Calibration of the Smoke Stain Reflectometer

The BS concentration was calculated from the reflectance measured in the paper filter (Whatman No. 1). The reflectance was measured by using the SSR. Before taking measurements, the instrument was calibrated according to the instruction manual published by the UK Department of the Environment, Transport and the Regions as described in (Loader, 1999). By using the plate provide by the suppliers, the expected values should be around 34 ± 1.5 %. The obtained values were in accordance with the plate transmittance values with an average of 34.2 %.

After plate calibration, the instrument was calibrated using the blank filter paper and before using it for the Teflon filter, it was calibrated again using a blank Teflon filter. The SSR was set at 100 %, after this, 5 blank filters were measured given total average percentages of 99.8.± 0.52 % (AM±SD). The Teflon filter average percentages were 100.3 ± 0.24 % (AM±SD). The filters were measured five times, in the center of the filter and in each of the corners (Molnar, 2007). The average of the five measurements was used in the calculations.

9.3.3 Analytical determination

9.3.3.1 Reflectance and Absorbance

The SSR method consists of measuring the darkness of the filter by the reflectance of the light (%) which is read by photocells (Dotse et al., 2012). The scale of measurement is from 0 to 100 % which goes from black to white. Though the SSR method is by reflection, according to the ISO9835, (1993) the absorbance (a= m^{-1}*10^{-5}) can be calculated. Using the reflectance, and applying Eq. IX-1 it is possible to have the absorbance (m^{-1}):

Eq. IX-1

$$a = \left(\frac{A}{2V}\right) \ln\left(\frac{R_0}{R_f}\right)$$

Where:

A, was the load filter area (m^2)

V= sample volume measured in m^3

R_0= reflectance of field blank

R_f= reflectance on sampled filter respectively (%) (Quincey, 2007, Cyrys et al., 2003, Minguillón et al., 2012).

9.3.3.2 Estimation of BS concentration

1) British Standard Smoke Calibration

Different formulae to calculate the BS can be found in the literature. (Loader, 1999) methodology used to calculate BS developed the British Standard Smoke Calibration Curve (BS 1747: Part 2: 1991) by using the SSR readings. The used formula depend on the reflectance reading. If the reflectance percentage was between 40 TO 99 % Eq. IX-2 was used:

Eq. IX-2

$$C = \frac{F}{V}(91679.22 - 3332.0460\,R + 49.618884R^2 - 0.35329778R^3 + 0.0009863435\,R^4)$$

Where:

C = concentration (µg m^{-3}), British Standard Smoke Calibration

V = volume of air sampled (for historical reasons this is in ft^3: to convert from metric, 1 m^3 =35.314667 ft^3) .

F = a factor relating to the sampler clamp size, in this case the clap size was1/2 inch so, the factor used was 0.288

R = reflectometer reading (%)

While for readings between 40 to 20 % Eq. IX-3 was applied:

Eq. IX-3

$$C = \frac{F}{V}(214245.1 - 15130.512R + 508.181R^2 - 8.831144R^3 + 0.0628057R^4)$$

2) BS index

In a study conducted by Quincey,(2007) the BS index (I_{BS}) was used to calculated BC concentration. In Eq. IX-4 the absorbance is considered to obtain as final result the Black Carbon (Eq. IX-5):

Eq. IX-4

$$I_{BS}\,(\mu g\ m^{-3}) = 3.46 \times 10^9 a^2 + 4.438\ \times\ 10^5 a$$

Where:

a= absorbance (m^{-1})

Eq. IX-5

$$C_{BC}\,[\mu g\ m^{-3}] = \sqrt{4.18\,I_{BS} + \ 59.6 -}\ 7.72$$

9.3.3.3 BC concentration

The real-time BC concentration data obtained from the MicroAeth™ Model AE51 was downloaded and post processed according to the methodology recommended by Hagler (2011). This uses the ONA algorithm correction method proposed by the US Environmental Protection Agency (EPA) which consists of averaging the time variable to cut down the noise in the data, and therefore correct negative values in the BC concentration (Hagler, 2011, Cheng and Lin, 2013).

To correct the light scattering, the formula proposed by Apte et al.,(2011) was applied (Eq. IX-6).

Eq. IX-6

$$BC = \frac{BC_o}{(0.88\,Tr + 0.12)}$$

Where:

BC= corrected BC concentration (ng m^{-3})

BC_0=uncorrected BC concentrations (ng m^{-3})

Tr = is the measured filter transmission (%)

The constant 0.88 and 0.12 are the slope and the intercept of the regression line.

Transmission is obtained by using the Attenuation (%) (ATN) which is the absorbance of the spot measured in the filter (AethLabs, 2012) and accumulation of the optical absorbing particles in the filter causes the increment in ATN (Eq. IX-7):

Eq. IX-7

$$Tr = \exp(-\frac{ATN}{100})$$

This formula has been used recently in some studies including Wang et al. (2011a) and Apte et al. (2011). Wang et al. (2011a) calculated BC concentration from road emissions in Beijing and corrected the BC data using the correction factor provided by Kirchestetter and Novakov (2007).

9.3.3.4 EC measurements

The quartz filters used to measure OC and EC were pre-heated at 600 °C for a period of 5 hours and stored in the freezer before and after sampling. The filters were analyzed using the Sunset Laboratory's Semi-Continuous OCEC instrument using European Supersites for Atmospheric Aerosol Research (EUSAAR II) protocol (Cavalli et al.,2010). The EC data was used to compare the relationship between the EC and the BC data from the MicroAethalometer and the reflectance form the Teflon filter. Previous studies show close relation between EC and BC (Lavanchy et al., 1999, Chow et al., 2009).

9.4 Results and discussion

The relationship of interest to establish whether the Teflon filter can be used as a filter media to calculate BC and therefore the BC particle size by using the MOUDI are the following:

- BC from MicroAethalometer with the reflectance from Teflon filters. The main purpose is to analyze the reflectance from Teflon filter collected in the MOUDI and convert this reflectance to BC.
- BS in the filter paper with the reflectance in the Teflon filter. The objective is to convert the reflectance of the Teflon filter used in the MOUDI to BS.
- EC in quartz filter with reflectance in the Teflon filter. The purpose is to convert the reflectance of the Teflon filter in the MOUDI to EC.

9.4.1 Reflectance

The percentage of transmittance depends on the darkness of the filter, and less dark filters had a higher percentage of reflectance. Therefore 100 % of the transmittance was considered as a white filter. Figure X-1 shows a plot of the reflectance measured on the filter paper against the Teflon filter in the samplings sites.

The percentages of reflectance in the Teflon filters were higher than in the filter paper (considering that the filter paper absorbed the PM while the Teflon filter kept a layer of the PM on the top of the filter). The regression shows a positive curvilinear correlation between both filters with an R^2= 0.96. One factor that may possibly affect the correlation might be the heterogeneous deposition which can cause a difference in the SSR results since only five points in the filter were measured.

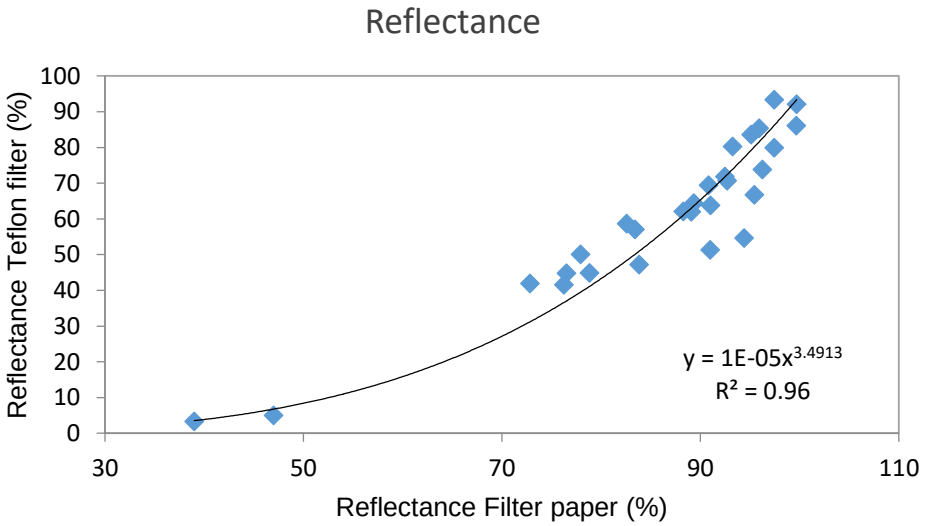


Figure IX-1 Relationship between reflectance in the filter paper and Teflon filter (%).

9.4.2 Absorbance

After calculating the reflectance, the absorption coefficient (absorbance) was calculated adopting the formula used by previous studies (Cyrys et al., 2003, Quincey, 2007, Minguillón et al., 2012) (Eq. IX-2).

The absorbance takes into consideration the volume of the sample, therefore variation in flow were corrected. Our main objective was to determine the BS, EC and BC from the Teflon filter by using the regression equation. For that reason, the relationship between reflectance and absorbance with these three measurements were compared to consider whether reflectance or absorbance was more useful measurement for our purpose . However, the first step in this analysis was to determine the relationship between filter paper and Teflon filter absorbance. Figure IX-2 show a good correlation between these two variables, with and an R^2= 0.83.

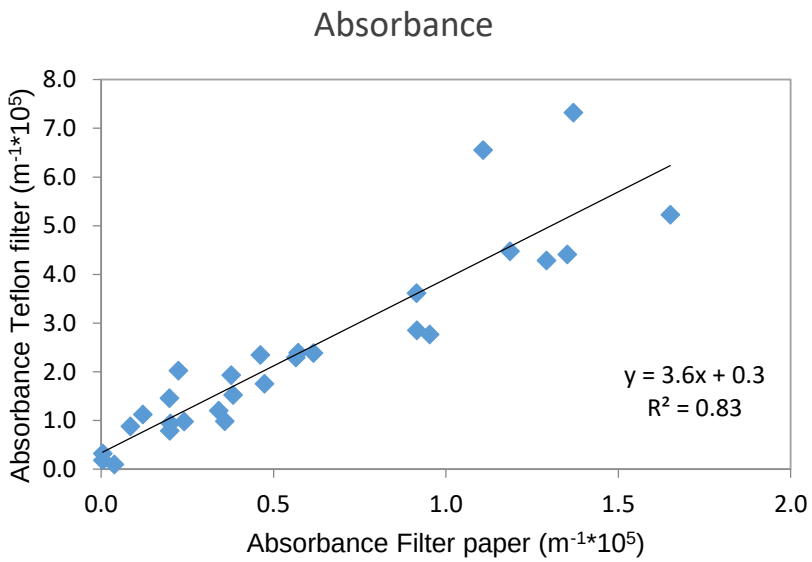


Figure IX-2 Relationship between absorbance in the Teflon and the paper filter ($m^{-1}*10^5$). The absorbance was multiplied by 10^5 for better understanding on the graph.

9.4.3 Black smoke and black carbon

To calculate the BS concentration from the SSR reading, the British Standard Smoke method, which calculations were created for a specific filter media, was used (Loader, 1999, Cyrys et al., 2003) (Eq. IX-2 and Eq. IX-3). Black smoke Index was also used to calculate the BS, (ISO 9835, 1993). This formula uses the absorbance and the BS standard tables, to calculate the black smoke index (Eq. IX-4) and finally Quincey (2007) uses a formula to determinate the BC (Eq. IX-5) by using the I_{BS}.

The BC calculated from the Quincey (2007) equation Eq. IX-6 shows high correlation with the BC from the AE51 (R^2=0.92) and with the British Standard Method (R^2=0.99) (Appendix 16).

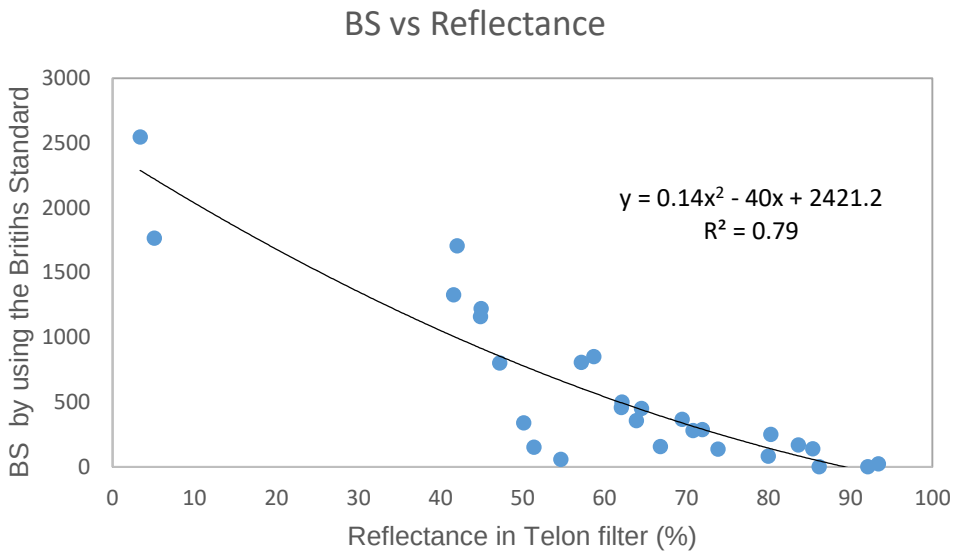


Figure IX-3 Relationship between the reflectance from the Teflon filter (Used in the MOUDI) and the BS calculate form the filter paper by using the British Smoke Stain Method (BS1747 part 2 1999).

Figure IX-3; shows the relationship between the reflectance of the Teflon filter and BS calculated by using the British standard, the relation displays an R^2 of 0.79. Low

reflectance percentage will have higher BS concentration as that can be observed clearly at the Marylebone site which reflectance percentage was less than 10.

A better relationship was observed between the absorbance in the Teflon filter and the BS calculated from the British Smoke Stain Method (paper filter) (Figure IX-4), in which, to calculate the absorbance the sampled volume was taken in consideration. This relationship displays an $R^2 = 0.95$. Therefore, at this point, to calculate the BS form the Teflon filter, it is recommended to apply the relationship between absorbance of Teflon filters and BS calculated by using the British Smoke Stain Method (BS, 1747part 2 1999).

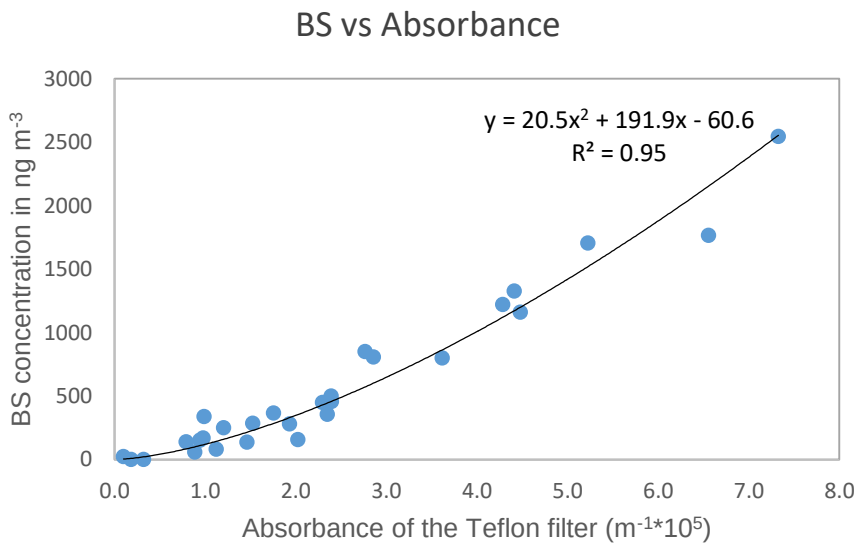


Figure IX-4 Relationship between the Absorbance in the Teflon filter and (used in the MOUDI) and the BS calculated from the filter paper by using the Smoke Stain Method (BS1747 part 2 1999). The absorbance was multiplied by 10^5 for better understanding on the graph.

9.4.4 MicroAethalometer

If the BS index equation takes into consideration the loading effect of the samples, which is influenced by the white light sources and penetration of the particles into the

filter (Quincey, 2007), then, the BS calculated in the previous section should be comparable with the BC obtained from the MicroAeth™ model AE51 (Quincey et al., 2011). There is a good relationship between the BC and the BS concentration calculated from the filter paper (R^2=0.82) (Appendix 16). However, since our objective is to convert reflectance or absorbance of the Teflon filters to BC, it is necessary to find the relationship between BC and the reflectance or absorbance of the Teflon filter (used in the MOUDI). The plot in Figure IX-5 shows that the relationship between reflectance of the Teflon filter and the BC measured in the MicroAethalometer has an R^2 of 0.94 and the absorbance was very similar (R^2 = 0.93) (Figure IX-6).

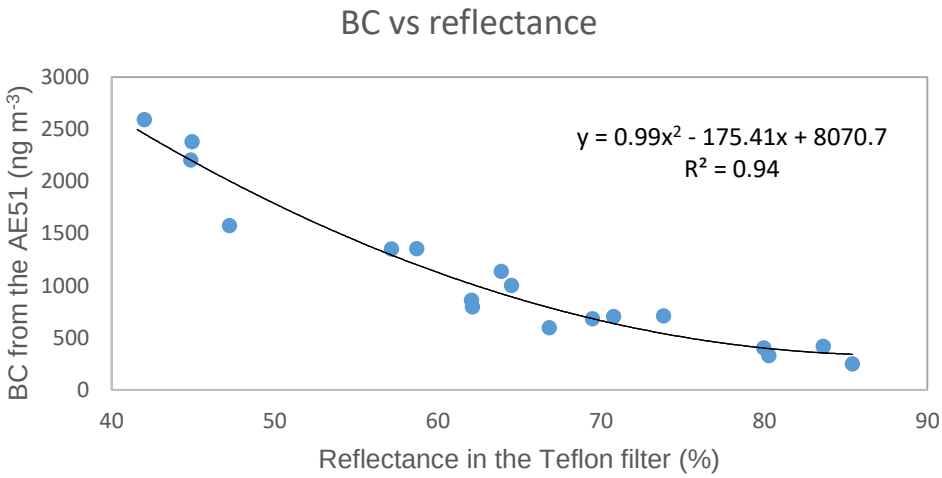


Figure IX-5 Relationship between the BC obtained from the MicroAethalometer and the Reflectance in the Teflon filter.

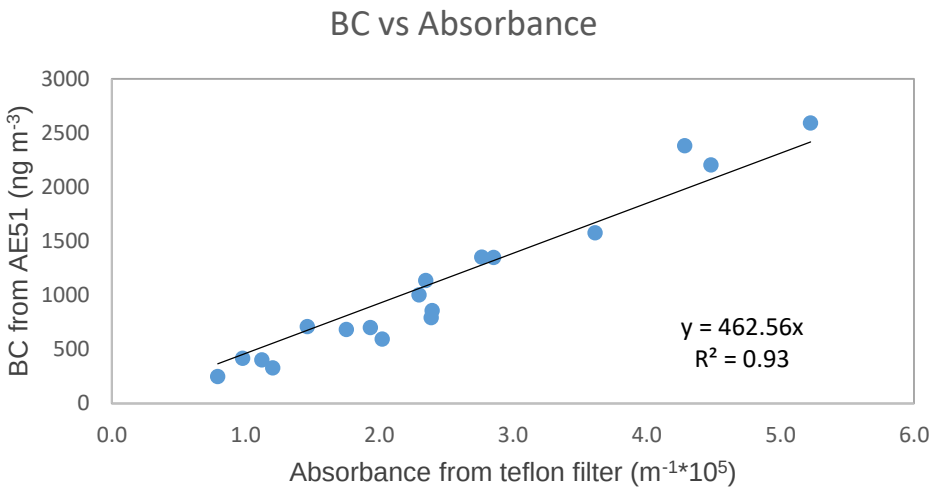


Figure IX-6 Relationship between the BC obtained from the MicroAethalometer and the absorbance in the Teflon filter. The absorbance was multiplied by 10^5 for better understanding on the graph.

9.4.5 OC/EC data

Several authors have reported agreement between the BC and EC data, with high correlation ($R^2 > 0.80$) between the two variables (Jeong et al., 2004, Hitzenberger et al., 2006, Bae et al., 2007, Snyder and Schauer, 2007, Ringuet et al., 2012). Our data is in agreement with previous findings, displaying an acceptable correlation (R^2=0.84) between the measurements (Figure IX-7).

However, the intercept beginning at 505.03 meaning that the expected values less than 508 will not meet the equation criteria as the relationship is locally linear. The EC data was also compared with the BS measurements using filter paper. Figure IX-8 shows a good relationship between both reporting an R^2 value of 0.77. Because some of the EC values from the ambient sites were missing, all the comparisons which involved EC were done only for BROS and EROS data.

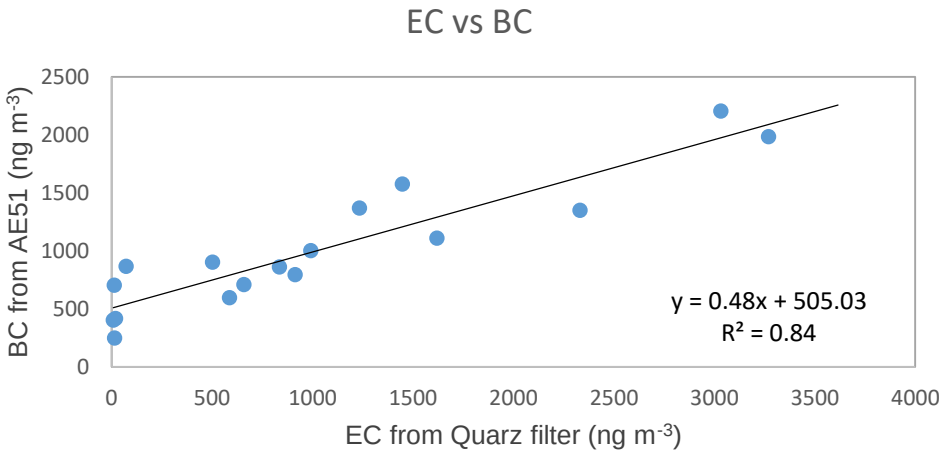


Figure IX-7 Comparison between the BC data obtained from the MicroAethalometer and the EC data.

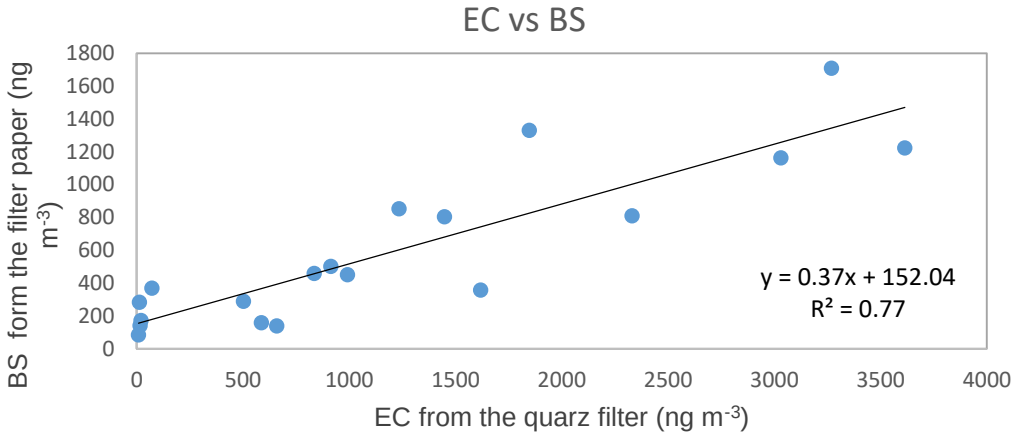


Figure IX-8 Correlation between the BS in the filter paper and the EC concentration.

One of the main relationships of our interest was between the EC with the reflectance or absorbance of the Teflon filter so we could convert the reflectance or absorbance of the Teflon filter used in the MOUDI into EC concentration. This relationship according to Figure IX-9 is good showing an R^2 of 0.77. However, the formula only applies for reflectance values between 20 and 85. Moreover, by comparing the absorption coefficient from the Teflon filter and the EC data a better relationship can be observed

as the reported r-squared was 0.81 (Figure IX-10). The interceptor value in the equation is negative, however; zero absorbance is less likely to be obtained. Therefore, the values of the constants can be trustily used. But by forcing the line to zero, clearly the line does not fit the slope; therefore the predicted values will be biased outside of the range.

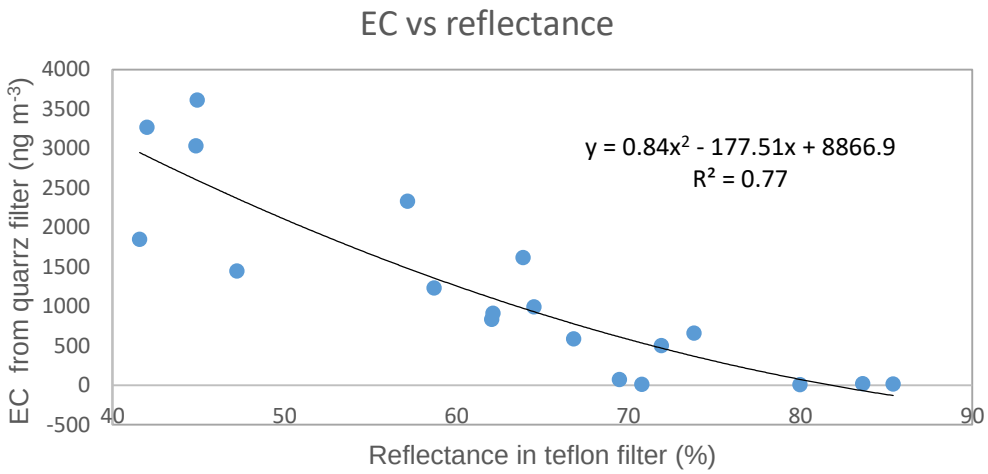


Figure IX-9 Relationship between the reflectance obtained from the Teflon filter (used in the MOUDI) and the EC concentration.

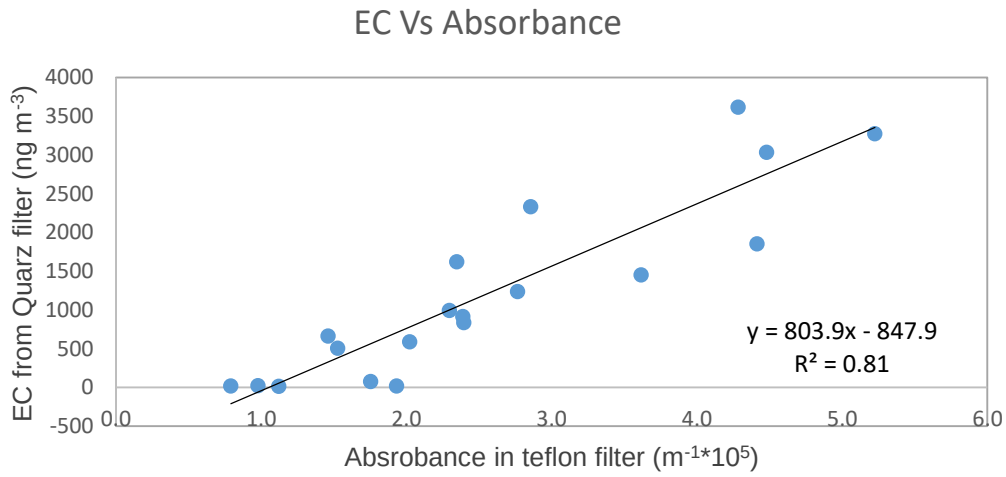


Figure IX-10 Correlation between the EC concentration and the absorbance in Teflon filter. The absorbance was multiplied by 10^5 for better understanding on the graph.

9.5 Conclusion

There is a good agreement between reflectance (R^2 =0.96) and the absorbance (R^2=83) in the comparison between the filter paper; used to measure BS, and the Teflon filter; used in the MOUDI.

BS concentration cannot be calculated for Teflon filter samples, because the proposed formulas are specific for the type of filter paper (Cyrys et al., 2003). For this reason this study compared the relationship between reflectance in the Teflon filter with the BS in the filter paper was analysed. A high correlation was observed (R^2=0.79), and this results supports the assumption that the reflectance can be used to obtain BS. However, a best fit was obtained for the relationship between Absorbance (Teflon filter) and the BS concentration (filter paper) with R^2 of 0.95. Our results suggest that, reflectance can be measurements on Teflon filters, and absorbance can be subsequently calculated, and this estimates (Figure IX-4) can be used to calculate BS from Teflon filters.

Previous researchers have postulated that BS and BC were design to express different properties of the aerosols. However correlation of BS and BC can be observed (Hitzenberger et al., 1999, Bae et al., 2007, Quincey, 2007, Quincey et al., 2011), and this is consistent with our results as high correlation was found between BC and BS (R^2=0.82)

Knowing that the relationship between BS and reflectance/ absorbance gave us good correlation and the same for BC and BS, the next comparison was focused on the BC obtained from the AE51 with the reflectance and absorbance, so we could convert reflectance or absorbance directly into BC. The results achieved in these relationships were similar to the obtained with the BS, reporting an R^2 of 0.92 and 0.94 respectively.

Researchers had also pointed the relationship between BS and EC (Lavanchy et al., 1999, Cyrys et al., 2003, Jeong et al., 2004, Hitzenberger et al., 2006, Snyder and Schauer, 2007, Quincey et al., 2009). The EC was calculated from the quartz filters and the results were compared with the BC and the BS. Good correlation between them was observed, reporting R^2 of 0.84 and 0.77 respectively. The reflectance and the absorbance from the Teflon filters were also compared with the EC results. High correlation was given in the comparison with the absorbance (R^2= 0.80). However, the interceptor was too high so values must not be predicted outside the range.

In conclusion reflectance and absorbance measurements in Teflon filters can be converted into BS, BC or EC (with exceptions) by using the regression equations discussed in section 9.4. However, absorbance measurements already produce high correlations.

CHAPTER X. BC SIZE DISTRIBUTION

10.1 Introduction

While there are many studies reporting mass particle size distributions, limited information is available on BC size distributions. Having a BC size data in different environments and personal exposure is essential to characterized human health since BC size distribution plays an important role in the exposure, relevant to human risk assessment, and useful to calculate inhalation rates and dose. Toxicological and epidemiological studies consider that the particle size distribution is important to characterized the exposure, however the fact that a wide range of size and methodologies had been published lead to less comparable and accurate results (Cao et al., 2012, Ning et al., 2013, Cheng et al., 2014).

Concentrations of BC increase as the particle size decrease and lung regional deposition depends on the particle size and the aerosol characteristics. Small particles will normally deposit in the lower airways (Carvalho et al., 2011). Particle size distribution might differ depending on the chemical composition and the ambient characteristics; therefore, to properly asses the risk at the personal level, BC size fraction distribution in different microenvironments typically visited during the daily routines should be considered (Lee and Dong, 2011, Wallace et al., 2011, Cao et al., 2012).

10.2 Objective

The objective of this study was to characterize the size distributions (SDs) for BC at several microenvironments that are most frequently visited by the FIXAT study volunteers.

10.3 Methodology

To determine the BC size distribution, size-segregated PM samples were collected in different microenvironments outdoor [BROS and EROS], office and home (Table X-1) using the rotating 10-stage Micro Orifice Uniform Deposit Impactor (MOUDI Model 110-R, MSP Corporation). The MOUDI was operated at 30 L min^{-1} for a period of 48 hr, and particles in the size range of 0.056 to 18 µm were collected using PTFE filters (Millipore 47 mm Teflon Membrane filter LCR hydrophilised, 0.5 µm pore size). In the event of a flow rate lower than 30 L min^{-1}, the cut points were corrected using Eq. X-1:

Eq. X-1

$$corrected\ D_p = D_p \sqrt{\frac{F_1}{F_2}}$$

Where:

D_p= nominal cut point (µm)

F_1=nominal flow rate (L min^{-1})

F_2 recorded flow rate (L min^{-1})

Table X-1 Sites and total of samples collected for 48hr sampling period.

Site	# samples
BROS	5
EROS	5
Office	3
Home	3

The MOUDI filters were analysed using the smoke stain reflectometer (SSR) to determine the percentage transmittance by using methodology reported in CHAPTER

IX (Loader, 1999).The transmittance was used to calculate the absorbance following the method ISO9835, (1993) described by (Quincey, 2007) using Eq. X-2.

Eq. X-2

$$a = \left(\frac{A}{2V}\right) \ln\left(\frac{R_0}{R_f}\right)$$

Where:

A, was the load filter area (m^2)

V= sample volume measured in m^3

R_0= reflectance of field blank

R_f= reflectance on sampled filter respectively (%) (Quincey, 2007, Cyrys et al., 2003, Minguillón et al., 2012).

The conversion factor obtained from the linear regression equation between the BC AE51 and the absorbance calculated from the Teflon filter equation in Figure IX-6 from chapter VIII, was used to finally obtain the BC concentrations by size (Eq. X-3).

Eq. X-3

BC= 426.28 (absorbance)

10.4 Results and discussion

After having the MOUDI filter, the reflectance (%) was obtained by using the SSR and following the SOP given by (Loader, 1999). Almost blank filters were obtained for high sizes at the four sample microenvironments; while small sizes displayed lower reflectance (more darkness filters) (Table X-2).

Table X-2 Reflectance obtained from the different location- and base on the MOUDI size.

	Reflectance			
size (µm)	BROS	EROS	Office	Home
0.056	59.4	85.1	49.9	52.7
0.10	73.2	91.4	58.6	67.6
0.18	93.3	96.8	88.3	93.4
0.32	92.6	97.7	93.1	94.3
0.56	97.6	98.6	98.6	97.9
1.0	96.6	98.7	98.3	97.9
1.8	98.9	99.1	99.2	99.1
10.0	98.9	98.8	98.9	98.9
18.0	98.7	99.9	99.0	99.1

After calculating the reflectance, the absorbance was obtained by using formula given by (Quincey, 2007), to finalizing with the BC concentration for each size fraction with considering the cut point correction (Table X-3). Average concentrations at EROS were higher than BROS, and office registered higher values than home. However, no significant statistical difference was observed between the different sampled microenvironments (one-way, ANOVA $p>0.05$).

Table X-3 BC size fraction concentration from four microenvironments (ng m^{-3}).

size	BROS		EROS		Office		Home	
(μm)	AM	SD	AM	SD	AM	SD	AM	SD
0.03	249.3	67.8	330.8	171.1	311.1	41.2	288.0	42.9
0.08	147.2	34.7	230.7	132.6	242.0	62.9	175.6	36.4
0.34	33.0	7.1	64.3	59.8	56.1	37.8	29.6	8.8
0.81	35.7	13.3	30.8	16.0	30.9	13.4	25.1	4.7
1.45	11.1	4.3	13.9	6.0	4.8	4.1	8.6	3.3
2.59	16.1	5.3	11.4	3.7	6.3	7.5	8.3	2.0
4.56	5.1	2.4	6.4	5.4	2.1	1.1	3.1	2.7
8.09	5.3	2.2	5.1	3.2	3.3	3.1	3.8	2.1
14.52	5.9	4.7	2.4	2.6	2.9	1.5	3.2	1.1
Total	**508.6**	**125.1**	**695.9**	**339.2**	**659.3**	**112.2**	**545.4**	**84.9**

10.4.1 BC size fraction distribution

In general, about 80 and 90 % of the total BC particles from Birmingham samples were found to be in the accumulation mode (0.03 to 0.3 μm) (Figure X-1), which is consistent with previous studies (Clarke et al., 2004, Reddington et al., 2013). (Cheng et al., 2014) indicated that the BC mass size distribution was dominant at the 0.16 μm in Taipei, Taiwan; while (Hitzenberger and Tohno, 2001) noted that the size mode distribution was between 0.15 and 0.39 μm for Uji, Japan. Traffic site BC mass size distribution was dominant between 0.11 to 0.36 μm for London, UK (Liu et al., 2014). Tailpipe BC measurements showed peak values at 0.1 and 0.15 μm, while ambient and road site exhibited the highest peak at 0.2 μm (Ning et al., 2013), traffic emission BC

concentrations reported two mode, high peak was show during the traffic hours (0.1 μm) and during the urban burning episode (0.2 -0.3 μm) For Tijuana, Mexico (Takahama et al., 2013).

Obtained results are in agreement with previous findings in which high concentration of BC are normally attributable to traffic emissions (Hitzenberger and Tohno, 2001, Clarke et al., 2004, Rissler et al., 2012, Ning et al., 2013, Reddington et al., 2013, Cheng et al., 2014, Liu et al., 2014, Takahama et al., 2014). Although, the primary peak concentration at the background site (231 ng m^{-3}) at 0.1 μm size was higher than the traffic site (147 ng m^{-3}), the difference is not significant (independent t-test $p>0.05$) and size followed the same trend. The secondary highest peak was in the accumulation mode (0.8 μm) with a mean concentration of 11.4 ng m^{-3} at the background site and 16.1 ng m^{-3} at the traffic road site (Figure X-1). This difference between the sites could be attributed to the influence of local winds as pollutant concentrations have been found to fluctuate with wind speed and direction (Kozawa et al., 2012, Perrone et al., 2013, Quiros et al., 2013, Cheng et al., 2014, Liu et al., 2014). Moreover, mean BC concentrations were lower than the previous obtained for Birmingham with 1.3 ± 2.2 μg m^{-3} (AM±SD) for personal exposure samples, while the sampling site (Birmingham Tyburn) had reported 0.91 ± 0.85 μg m^{-3} (Delgado-Saborit, 2012). It is important to note that during the five-day MOUDI sampling campaign, heavy rain/wind were registered for two days and moderate rain for other two days.

The mean total BC concentration at the traffic site (509 ng m^{-3}) and background site (595 ng m^{-3}) were lower than the reported concentrations (2800 ng m^{-3}) for Beijing, China (Cheng et al., 2014), and 4500 and 5000 ng m^{-3} for Uji, Japan and Vienna,

Austria respectively (Hitzenberger and Tohno, 2001). In Mexico, at the border city, the reported concentrations were 1800 ng m^{-3} (Takahama et al., 2013). Diesel emissions measurements showed an average BC concentration between 173 to 19 µg m^{-3} (Ning et al., 2013).

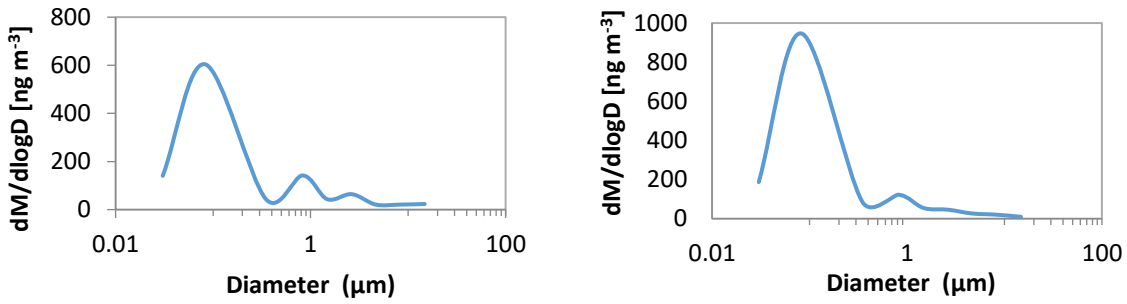


Figure X-1 BC particle size fraction distribution a two outdoor sites, a) trafficked site and b) background site.

The comparison between the home and office particle size distribution showed no statistical difference for particles less than 0.1 µm (0.08 µm) and the masses for primary peaks were 242 and 145 ng m^{-3} respectively (Figure X-2). The secondary peak was observed at 0.8 µm with an average concentration of 6.3 ng m^{-3} for home and 8.3 ng m^{-3} for office. No house activities were registered during the sampling days and according to the literature, biomass burring or cooking contribute to high concentration and the BC particles which diameter lie between 0.21-0.30 µm. Residential heating is also considered a contributor of the BC concentration and samples were taken during the summer period, therefore burning emissions were absent (Schwarz et al., 2008, Liu et al., 2014, Takahama et al., 2014).

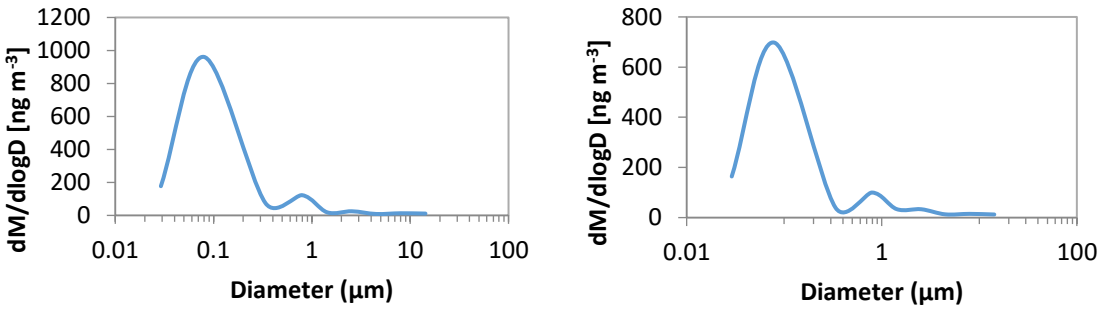


Figure X-2 BC particle size fraction distribution at two indoor sites, a) home and b) office.

Information about BC mass size fraction distribution at the indoors was not previously found. However total BC concentration obtained for house (547 ng m^{-3}) and office (659 ng m^{-3}) were lower than previously reported values. For instance, BC concentrations reported for New York houses were 1590 and 1160 ng m^{-3} (Cornell et al., 2012) and (Dons et al., 2011) found that home concentration were almost similar to work with 1223 ng m^{-3} and 1276 ng m^{-3} respectively. By sampling the home area, (Van Vliet et al., 2013) reported average concentrations of 2000 ng m^{-3} while in Birmingham, UK earlier measurements for indoor microenvironments reported average concentration of 950 ng m^{-3} for home and 2900 ng m^{-3} for office (Delgado-Saborit, 2012).

10.5 Conclusion

BC size distributions were obtained from different indoor and outdoor microenvironments. The outdoor sites displayed a similar BC size distribution, with some differences in the average concentration. Higher concentration was observed at the background site, and plausible factors contributing to this include inlet location or obstruction of the flow. Home concentrations were found not to be statistically different from the office; this might be attributable to the indoor home activities which were almost null. The BC size fraction showed a bimodal distribution with a primary peak observed at 0.08 µm and second at 0.8 µm for all the sampled locations.

10.6 Recommendations

A longer sampling period (e.g. one year) should be considered to eliminate the seasonal bias and even more if it is possible daily or hourly bias to determine the temporal variability in the peaks. Also, to have more accurate data for the epidemiology studies, a range of offices and homes should be considered to take into account all the factors that contribute to indoor BC (e.g. Occupancy, heating system, ventilation and location of the houses/office). New portable technology should be considered to collect BC particle size distribution in indoor microenvironments to avoid the noise inconvenience of big instruments indoors.

CHAPTER XI. LUNG DEPOSITION

11.1 Introduction

Air pollution has been associated with adverse health effects (Strak et al., 2010, Knibbs et al., 2011, Rohr and Wyzga, 2012) which are primarily caused by the chemical and physical composition of the air (Int Panis et al., 2010). PM has been well documented to be one of the major air pollutants that affects human health, which primary source is the vehicular combustion emissions (Choi et al., 2012, Janssen et al., 2013, Yang et al., 2013). Exposure to PM has been associated with cardiovascular mortality and morbidity (Berico et al., 1997, Shi et al., 1999, Du et al., 2010, Long et al., 2011, Ham et al., 2011, Wheeler et al., 2011, Wu et al., 2012a, Manigrasso and Avino, 2012). Although particulates play an important role in human health, what actually matters apart from the PM mass, is the PM composition (Rohr and Wyzga, 2012). Recently, there has been a surge in interest on BC, since a high association has been reported between BC and adverse health effects (Janssen et al., 2011, Suglia et al., 2008b).

To get a picture of the role of BC and PM in human health effects, it is important to consider the particles deposited in the respiratory tract. Researchers have focused on determining the fraction of particle size distribution and the deposition dose, however less information was found about BC size distribution and much less about the BC deposition dose.

Some studies had found that ultrafine particles are more associated with lung function decrements than large particles (Zhang et al., 2005, Löndahl et al., 2006, de Hartog et al., 2010, Du et al., 2010).

11.1.1 Deposition mechanisms to inhaled fraction factors

11.1.1.1 Physical and chemical constitution

This property of the aerosol includes the particle diameter (Zhang et al., 2005, Berico et al., 1997, Löndahl et al., 2009) shape, density and the hygroscopicity of the particle (Figure XI-1). Asgharian (2004) created a model to calculate the deposition of hygroscopic particles, assuming that these particles may change in size as they travel through the lung and it might influence the deposition site and the amount. Löndahl et al., (2009) reported that the shift of the deposition is higher for the more hygroscopic group and attributed this to particle growth due to absorption of water vapour. The chemical reactivity also affects the deposition factor and can cause different effects in each of the lung sections (Salvatore, 2003, Löndahl et al., 2009, Martins et al., 2010).

11.1.1.2 Subject exposure condition

Other factors that might affect the inhalation and deposition can be the subject exposure condition, such as the temperature and the air velocity (See and Rajasekhar, 2006, Ham et al., 2011). Previous studies have highlighted the role of seasonal variations, with higher deposition efficiencies reported during summer compared in winter in all the regions of the respiratory tract (Ham et al., 2011). Differences have also been found between indoor (Long et al., 2011), and outdoor environments (Frosig and Sherson, 1997, Yassin et al., 2012). The physiologic demand of the subject will alter the deposition fraction and differences can be found in subjects walking or cycling compared with those who drive. On the other hand, the type of work will demand either high or low physical activity, this is the case of hard work compared with office work (Int Panis et al., 2010).

11.1.1.3 Individual characteristics

Lung deposition also depends on individual characteristics such as age and gender as well as other factors such body size, overall health, smoking status are other factors affecting the lung deposition (Bailey 1994, Salvatore, 2003, Chio and Liao, 2008, Carvalho et al., 2011). A summary of key factors is presented in Figure XI-1

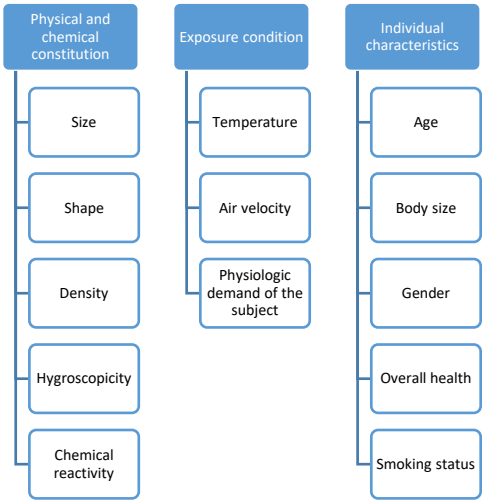


Figure XI-1 Factors that influence the inhalation and lung deposition.

11.1.2 Mechanism of Lung Deposition

During breathing, a volume of air comes near the face and is in contact with the nose or the mouth. This is ascribed as a breathing zone, (Salvatore, 2003) where small particles will be inhaled.

Particles larger than 10 µm, can be deposited in the nasal region but if the particle is coated with hygroscopic materials, there is a possibility to be captured into the nasopharyngeal (NP) region (Salvatore, 2003), by inertial deposition (Zhang et al., 2005), which is the most significant deposition mechanism in the NP region. Particles with an aerodynamic diameter less than 10 µm can be captured in the tracheobronchial (TB) region by sedimentation. Finally, particles that cannot be retained in the TB region

will penetrate to the pulmonary region, where they can be deposited in the bronchioles, alveolar ducts and the alveolar sacs. These particles are the respirable fraction (Zhang et al., 2005) the dominant deposition mechanism are sedimentation or diffusion, however particles with sufficient electric charge can be deposited by attractive electrostatic image forces (Salvatore, 2003).

11.1.3 Models to calculate the lung dose deposition

The International Commission on Radiological Protection (ICRP) model was developed by the Task Group of Human Respiratory Tract models for radiological protection. This model gives reference values for children of 3 months to 1 year, 5, 10 and 15 years old groups and adults. The model takes into account the difference in sensitivity of the respiratory tract tissue and the wide range of doses that might be received. Another feature of this model is that it uses five regions of the respiratory system: extrathoracic anterior nose (ET_1), extrathoracic posterior nasal passage (ET_2), bronchial (BB), bronchiolar (bb) and alveolar-interstitial (AI) (Bailey 1994) and these regions were divided based primarily on radiobiological consideration. However, it is important to note that the difference in function, deposition and clearance was also taken into consideration (Bailey 1994).

The Lung Dose Evaluation Program (LUDEP) model is a computer program, which enables calculation of dose in all the organs of the body. It includes an option to calculate lung dose based on the ICRP, but it is also possible to insert or change the parameters directly (Birchall et al., 1991). The LUPED model implements the model of the human respiratory tract (ICRP) and is used to calculate the deposition efficiencies (%) of inhaled particles in the human respiratory tract.

The Multiple-Path Particle Dosimeter (MPPD) is a computational dosimeter model developed by the Chemical Industry Institute of Toxicology (CIIT), currently The Hamner Institutes for Health Sciences and the Dutch National Institute for Public Health and the Environment (RIVM)

(Chio and Liao, 2008, Ham et al., 2011). The model calculates the deposition and clearance of monodisperse and polydisperse aerosols in the respiratory tracts of rats and human adults and children (deposition only) for particles ranging in size from ultrafine (0.01 µm) to coarse (20 µm). This model has been used to calculate the specific fractional deposition for PM in Taiwan where adults, youth and infants were sampled (Chio and Liao, 2008). The model has also been used to calculate the airway deposition in Fresno, California to determine seasonal variability of particle deposition (Ham et al., 2011) and to assess the potential health effect of the aerosols in Brazil (Martins et al., 2010).

A multiple path model was created by (Angilvel and Agharioan 1995) which was based on the single path deposition model developed by Schum and Yeh (1979). The modifications were basically that the deposition was calculated for every airway, which permitted to assess the variation in dose in different sites in the lung. Then, Asgharian, (2004) used the multi path model to create a mathematical model for the deposition of hygroscopic particles in asymmetric lung geometries of humans.

The Council on Radiation Protection and Measurements (NCRP) developed a model for the inhalation of radioactive substances in which they calculated the deposition and retention. This model was created as a contribution of the ICRP model (Wang, 2011). The model takes into account three main regions in the respiratory track, which are the

naso-oro-pharyngo-laryngeal region with 16 generation of airways, the tracheobronchial region, with 8 generation and the alveoli, and the pulmonary region. The generation in the regions are connected in series (Yeh et al., 1996).

11.2 Objectives

The aim of this study was to determine the BC particle size distributions for FIXAT BC concentrations, estimate the deposition efficiencies following the ICRP model for Caucasian adult subject in the four level of exercise; and calculate the DE for some of the activities developed by the FIXAT subject considering the size fraction and estimate BC deposition dose using the ICRP model.

11.3 Methodology

11.3.1 Deposited dose

Using the obtained data Eq. XI-1 was solved for each 5 min average sampling time given by the AE51 from the FIXAT samples. The deposited mass was calculated for each region of the respiratory system and per activity (Patlolla et al., 2010, Rissler et al., 2012, Hussein et al., 2013). The flow chat given in Figure XI-1 shows more information about data organization on the spreadsheet. Data was analysed using SPSS 21. To determine gender difference, an independent t-test was used. The ANOVA test was used for inter-comparison of microenvironments. To determine the deposited dose, several assumptions were established such as spherical particle shape, a unit of density, nose breath pattern.

Eq. XI-1

$$DD = \frac{C * VE * DE * T}{B_W}$$

Where:

DD= deposited dose (ng kg^{-1})

C= air concentration on each size fraction (ng m^{-3})
VE= ventilation rate (m^{-3} min^{-1})
DE= deposition efficiency at specific size fraction and gender
T= duration of the exposure (min)
B_w= body weigth (kg)

To calculate the deposited dose an Excel spread sheet was prepared with the DE which were calculated for the BC size distribution fraction obtained in CHAPTER X, concentration in each size (C) was calculated by using the size of the BC concentration given in table X-3 and assuming that the total BC obtained from the AE51 distribution was similar to the sampling sites. Ventilation rates (VE) used were the given by the ICRP model and observed in section 11.3.2, the sampling time (T) was obtained from the TAD considered the original time spent in each activity and the Body weight (Bw) obtained from the screening questionnaire (Appendix 8).

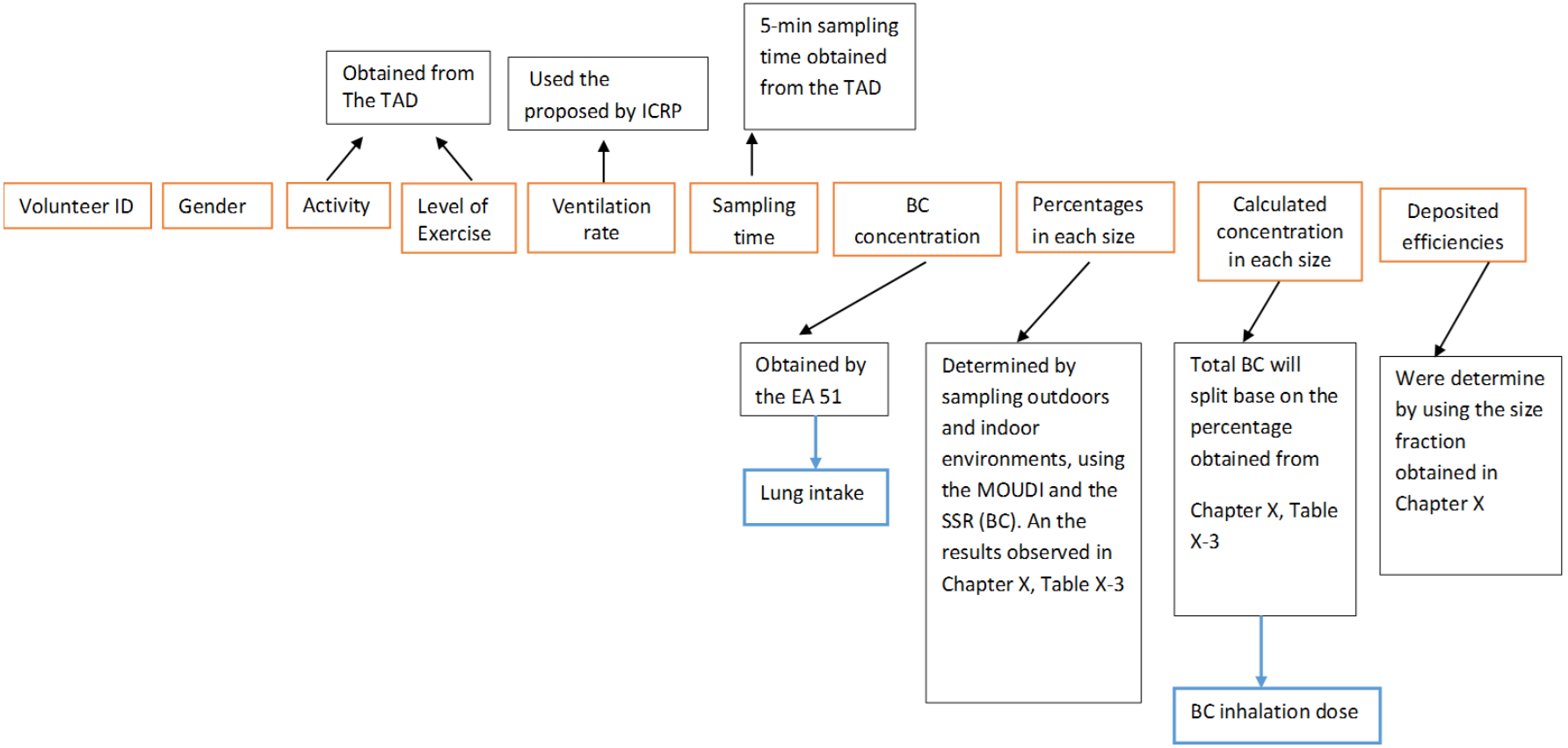


Figure XI-2 Flowchart describing the steps followed to calculate BC deposited dose.

11.3.2 BC Size Distribution

By using the information obtained in CHAPTER X, in which the BC size fraction distribution for four microenvironments was reported, the percentage of BC in each size bin was calculated for the four sampling sites. Subsequently, the percentage was extrapolated to split the total BC obtained from the AE51 FIXAT samples in different size fractions.

The assignment of the four microenvironments percentage in the activity performed by FIXAT volunteers was designated depending on the similarities of the environments details in Table XI-1. By doing this procedure at the end, we had FIXAT BC size fraction distribution. Assuming that the size fraction would be similar obtained in CHAPTER X for four microenvironments.

Table XI-1 General sites representative of microenvironments relevant to volunteers activities.

BROS (traffic roadside)	**EROS (background site)**	**Office**	**Home**
Walking / cycling in trafficked roads	Walking/ cycling in Background roads	Work Educational place	Indoor
Bus	Train	Conference centre	
Car	Park/ reservoir/canal garden	Office common rooms Laboratory Library/nursery	

11.3.3 Ventilation rate (VE) sensitive analysis

The amount of air that enters the human respiratory system can be calculated by measuring the tidal volume of air per minute. The amount of inhaled air depends on different characteristics such gender, age, level of exercise, subjects weight and health (Int Panis et al., 2010).

To determine which VE will be the most appropriate for the lung dose calculations a sensitivity analysis calculation of lung intake was calculated by using three different reported VE. The FIXAT VE were obtained according to the activities reported in the TAD by using the VE reported by (Allan and Richardson, 1998) and to the list was added to the VE obtained by (Int Panis et al., 2010) (Table XI-2). The ICRP model ventilation rates described in Table XI-3, were used considering only the values for adults as the sampling population were all adults. Values were assigned based on the level of exercise reported by the FIXAT volunteers in the TAD questionnaire.

Table XI-2 Ventilation rates (L min^{-1}) obtained from different activities and gender classification (Allan and Richardson, 1998).

Activity	Male adults	Female adults
Sleep	8.3	7.5
Home-based activities / Eat / Education	10.5	12.5
Work / Social / Other / Service related activities / Bring/get goods/people	16.1	13.0
Leisure / Daily shopping / Non-daily shopping	30.2	23.2
On foot	49.2	39.8
Train / Bus / Light rail / Metro	16.1	13.0
Car driver / Car passenger *	13.4	11.3
Bike *	59.1	46.2

* ventilation rates calculated by (Int Panis et al., 2010).

Table XI-3 Ventilation rates proposed by the ICRP model (L min^{-1})(ICRP, 1994).

		Resting	Sitting awake	Light exercise	Heavy exercise
VE	Male	7.5	9	25	49
	Female	5.3	6.4	20.8	45
Volunteer FIXAT activities		sleeping	Eating Working Relaxing Reading Computer work On bus On car On train Restaurant/pub	Walking Dusting/tiding Cooking Indoor /outdoor activities	Cycling Gym Running Clean (vacuum

A less robust classification was given by (Löndahl et al., 2007) in which only rest and exercise were considered. Therefore, the volunteer's FIXAT activities were classified based on these two characteristics (Table XI-4). For this classification, work was considered as resting as all the volunteers reported to work at office.

Table XI-4 Classification of the volunteers activities within the two levels of exercise (L min^{-1}) (Loader, 1999).

VE	Rest	Exercise
Male	9.45	39.5
Female	8.17	28.1
Volunteer activities	Eating	Indoor activities
	Relaxing	Cooking
	Sleeping	Walking
	Waiting	Cycling
	Travel by bus, car or train	Shopping
	Socializing	Tidying
	Working	Lab work
	Computer work	Cleaning
	Driving	Gardening
	Reading	

11.3.4 Lung intake

The lung intake (LI) or intake fraction was calculated using the BC FIXAT concentration (ng m^{-3}) in a determinate activity and the ventilation rate (m^3 min^{-1}) assigned for a specific subject activity (Eq. XI-2). The total BC mass lung intake (ng) for the general microenvironments was graphically analysed (Du et al., 2012).

Eq. XI-2

$$LI = VE * C * T$$

Where:

LI= Lung intake (ng)

C= concentration (ng m^{-3})

VE= ventilation rate (m^3 min^{-1})

T= time of exposure (min)

11.3.5 Inhalation dose

By using the VE and size fraction concentration, it is possible to calculate the inhalation dose (ID) (Eq. XI-5), and if the body weight is available it can also be added to have the final mass/ weight ratio. Before calculating the ID, it was necessary to determine the mass concentration of BC in the inhaled air (C_{inh}) by using Eq. **XI-3**.

Eq. XI-3

$$C_{inh} = IF * C_{air}$$

Where:

C_{inh}= concentration of inhaled air (ng m^{-3})

IF= inhalable fraction

C_{air}= size fraction air concentration (ng m^{-3})

The inhalable fraction (IF) is calculated by using Eq. XI-4. In which the particle fraction size diameter is incorporated to the fraction of a dust cloud that can be breathed into the nose or mouth.

Eq. XI-4

$$IF = 1 - 0.5\left(1 - \frac{1}{1 + 0.00076 d_p^{2.8}}\right)$$

Where d_p= size fraction (μm)

The inhalation dose (ID) then was calculated by using equation (Eq. XI-5)

Eq. XI-5

$$ID = \frac{C_{inh} * VE * T}{B_w}$$

Where:

ID= inhalation dose (ng $kg^{-1}day^{-1}$)

C_{inh}= concentration of PM in the inhaled air (ng m^{-3})

VE= ventilation rate (m^3 min^{-1})

T= time of exposure (min)

B_w= body weight (Kg)

11.3.6 Deposition efficiencies

The ICRP model considers the level of activity, gender, breathing rate, tidal volume, breathing frequency, and functional reserve capacity, with other parameters to calculate the deposition efficiency (DE) (Bailey 1994). However, for our purposes, the DEs were calculated by assuming a normal nose breath for an adult. To have the DE from different levels of exercises and gender, the reference values for regional deposition given in annex F of the ICRP annals publication 66 were used (ICRP, 1994). However, these tables report the DE only for some of the sizes; and MOUDI displayed

the results in different sizes (Table XI-5). Therefore, the ICRP reference values for DE were plotted to obtain an equation and calculate the DE at specific given size. The equations were for all the lung regions (ET, BB, Al and total) can be observed in Table XI-6 for male and Table XI-7 for female. The DE were assigned based on the level of exercise reported by the volunteers activities in the TAD, as the ICRP model gave DE for sitting, low and heavy exercise and sleeping.

Table XI-5 Particle size nominal and mean Dp distribution and mean diameter for MOUDI.

MOUDI nominal size	MOUDI Mean Dp
0.056	0.03
0.1	0.08
0.56	0.34
1	0.81
1.8	1.45
3.2	2.59
5.6	4.56
10	8.09
18	14.52

Table XI-6 Equations to calculate DE for a normal nose breath for male.

	ET1	ET2	BB slow	bb slow	AL	Total
Sleeping	$y = 0.0002x^3 - 0.0065x^2 + 0.0776x + 0.02$ $R^2 = 0.98$	$y = 0.0002x^3 - 0.0081x^2 + 0.0945x + 0.0249$ $R^2 = 0.97$	$y = -0.000006x^4 + 0.0003x^3 – 0.0041x^2 + 0.0206x + 0.0043$ $R^2 = 0.95$	$y = -0.000006x^4 + 0.0003x^3 – 0.0041x^2 + 0.0206x + 0.0043$ $R^2 = 0.99$	$y = 3E-05x^3 - 0.0007x^2 - 0.0047x + 0.1486$ $R^2 = 0.97$	$y = -0.000006x^4 + 0.0003x^3 - 0.0041x^2 + 0.0206x + 0.0043$ $R^2 = 0.95$
Sitting	$y = -6E-06x^4 + 0.0003x^3 - 0.0041x^2 + 0.0206x + 0.0043$ $R^2 = 0.99$	$y = 3E-06x^5 - 0.0002x^4 + 0.0033x^3 - 0.0355x^2 + 0.1841x - 0.025$ $R^2 = 0.99$	$y = -5E-07x^4 + 2E-05x^3 - 0.0003x^2 + 0.0014x + 0.0028$ $R^2 = 0.98$	$y = 5E-05x^2 - 0.0017x + 0.0163$ $R^2 = 0.98$	$y = 0.0003x^2 - 0.0144x + 0.1659$ $R^2 = 0.98$	$y = -5E-05x^4 + 0.0024x^3 - 0.0401x^2 + 0.2664x + 0.1846$ $R^2 = 0.99$
Light exercise	$y = -0.00003x^4 + 0.0014x^3 - 0.0224x^2 + 0.1454x + 0.0422$ $R^2 = 0.98$	$y = 0.00004x^4 + 0.0018x^3 - 0.0286x^2 + 0.1772x + 0.0619$ $R^2 = 0.97$	$y = -0.000001x^4 + 5E-05x^3 - 0.0007x^2 + 0.0031x + 0.003$ $R^2 = 0.98$	$y = 0.0000004x^4 - 2E-05x^3 + 0.0003x^2 - 0.0026x + 0.0103$ $R^2 = 0.97$	$y = -0.00007x^4 + 0.0031x^3 - 0.0493x^2 + 0.3x + 0.2526$ $R^2 = 0.97$	$y = -0.00007x^4 + 0.0031x^3 - 0.0493x^2 + 0.3x + 0.2526$ $R^2 = 0.99$
Heavy exercise	$y = 0.0001x^3 - 0.004x^2 + 0.0438x + 0.0428$ $R^2 = 0.94$	$y = 0.0002x^3 - 0.0087x^2 + 0.1074x + 0.0396$ $R^2 = 0.98$	$y = -0.000006x^4 + 0.0003x^3 - 0.0041x^2 + 0.021x + 0.003$ $R^2 = 0.95$	$y = -0.0000009x^4 + 4E-05x^3 - 0.0006x^2 + 0.0026x + 0.0074$ $R^2 = 0.98$	$y = 0.0004x^2 - 0.013x + 0.1308$ $R^2 = 0.99$	$y = -0.00006x^4 + 0.0028x^3 - 0.0453x^2 + 0.2911x + 0.1594$ $R^2 = 0.99$

Y= Deposition efficiency
X= particle size (μm)

Table XI-7 Equations to calculate DE for a normal nose breath for female.

	ET1	ET2	BB slow	bb slow	AL	Total
Sleeping	$y = 0.0002x^3 - 0.0061x^2 + 0.0744x + 0.0192$ $R^2 = 0.99$	$y = 0.0002x^3 - 0.0079x^2 + 0.0924x + 0.0163$ $R^2 = 0.98$	$y = -0.000006x^4 + 0.0003x^3 - 0.0041x^2 + 0.0206x + 0.0043$ $R^2 = 0.95$	$y = -0.0000006x^4 + 0.00003x^3 - 0.0004x^2 + 0.0017x + 0.008$ $R^2 = 0.99$	$y = -1E-05x^4 + 0.0005x^3 - 0.0064x^2 + 0.0201x + 0.1236$ $R^2 = 0.98$	$y = 0.0004x^3 - 0.0154x^2 + 0.1674x + 0.2379$ $R^2 = 0.95$
Sitting	$y = 0.0002x^3 - 0.0062x^2 + 0.0764x + 0.0278$ $R^2 = 0.98$	$y = 0.0002x^3 - 0.0084x^2 + 0.0965x + 0.0289$ $R^2 = 0.97$	$y = -0.0000003x^4 + 0.00001x^3 - 0.0002x^2 + 0.0009x + 0.0032$ $R^2 = 0.99$	$y = -0.000002x^3 + 0.0001x^2 - 0.0022x + 0.019$ $R^2 = 0.99$	$y = 0.00002x^3 - 0.0005x^2 - 0.005x + 0.1308$ $R^2 = 0.97$	$y = 0.0004x^3 - 0.0154x^2 + 0.168x + 0.2336$ $R^2 = 0.99$
Light exercise	$y = 0.0002x^3 - 0.0081x^2 + 0.0878x + 0.0877$ $R^2 = 0.93$	$y = 0.0003x^3 - 0.0102x^2 + 0.104x + 0.1198$ $R^2 = 0.89$	$y = 0.0000002x^5 – 0.00001x^4 + 0.0002x^3 - 0.0016x^2 + 0.0052x + 0.002$ $R^2 = 0.99$	$y = -0.0000001x^5 + 0.000008x^4 - 0.0001x^3 + 0.0013x^2 - 0.0053x + 0.0125$ $R^2 = 0.98$	$y = -0.0000004x^5 + 0.00002x^4 - 0.0005x^3 + 0.0052x^2 - 0.0345x + 0.1327$ $R^2 = 0.99$	$y = -0.00007x^4 + 0.0031x^3 - 0.0498x^2 + 0.3018x + 0.2548$ $R^2 = 0.97$
Heavy exercise	$y = 0.0001x^3 - 0.0041x^2 + 0.0446x + 0.0467$ $R^2 = 0.93$	$y = 0.0002x^3 - 0.0089x^2 + 0.1093x + 0.0478$ $R^2 = 0.98$	$y = -0.000006x^4 + 0.0003x^3 - 0.0041x^2 + 0.0206x + 0.0043$ $R^2 = 0.92$	$y = -0.0000006x^4 + 0.00003x^3 - 0.0004x^2 + 0.0017x + 0.008$ $R^2 = 0.99$	$y = -0.000003x^4 + 0.0001x^3 - 0.001x^2 - 0.0064x + 0.1095$ $R^2 = 0.99$	$y = -0.00006x^4 + 0.0028x^3 - 0.0458x^2 + 0.2949x + 0.153$ $R^2 = 0.99$

Y= Deposition efficiency
X= particle size (μm

11.4 Results

11.4.1 Size distribution

To have FIXAT BC size distribution, it was necessary first to calculate the fraction BC size distribution in each MOUDI bin, which are displayed in Table XI-8. Total FIXAT BC was split based on the MOUDI percentage and considering the classification given in Table XI-1. Therefore, the Excel sheet was constructed as observed in Table XI-9.

Table XI-8 MOUDI BC fraction percentage (%).

Size fraction	BROSS		EROS		OFFICE		HOME	
(µm)	dM/dlog D ng m^{-3}	%	dM/dlogD ng m^{-3}	%	dM/dlog D ng m^{-3}	%	dM/dlog D ng m^{-3}	%
0.03	140	12.7	187	12.5	177	12.5	164	14.8
0.08	604	54.8	947	63.2	961	68.0	698	62.9
0.34	44	4.0	86	5.7	75	5.3	40	3.6
0.81	142	12.9	122	8.2	123	8.7	100	9.0
1.45	44	3.9	54	3.6	19	1.3	34	3.0
2.59	64	5.8	46	3.1	25	1.8	33	3.0
4.56	21	1.9	26	1.8	9	0.6	13	1.2
8.09	21	1.9	20	1.4	13	0.9	15	1.3
14.52	23	2.1	9	0.6	11	0.8	12	1.1
total	1103		1498		1412		1108	

The BC size distribution from FIXAT samples (PE) was calculated assuming that the particles will follow the same distribution than those obtained from EROS, BROS, office and home (Table XI-8). The total BC concentration was split by size fractions and the percentages were assigned as describe in Table XI-1. The size concentration of BC particles shows a primary peak at around 0.1 µm for all the microenvironments.

Table XI-9 BC particle fraction size determination example.

subject activity	Total BC[(a)] (ng m^{-3})	MOUDI BC fraction percentage (%) from Table XI-8									Total BC concentration split in size (ng m^{-3})								
		0.03	0.08	0.34	0.81	1.45	2.59	4.56	8.09	14.5	0.03	0.08	0.34	0.81	1.45	2.59	4.56	8.09	14.5
		(µm)									(µm)								
home	759	14.8	62.9	3.6	9.0	3.0	3.0	1.2	1.3	1.1	112	478	27	68	23	23	9	10	8
home	760	14.8	62.9	3.6	9.0	3.0	3.0	1.2	1.3	1.1	112	478	27	68	23	23	9	10	8
home	750	14.8	62.9	3.6	9.0	3.0	3.0	1.2	1.3	1.1	111	472	27	68	23	23	9	10	8
home	835	14.8	62.9	3.6	9.0	3.0	3.0	1.2	1.3	1.1	124	526	30	75	25	25	10	11	9
Car	715	12.7	54.8	4.0	12.9	3.9	5.8	1.9	1.9	2.1	91	391	28	92	28	42	14	14	15
Car	1219	12.7	54.8	4.0	12.9	3.9	5.8	1.9	1.9	2.1	155	668	48	157	48	71	23	23	26
Car	2376	12.7	54.8	4.0	12.9	3.9	5.8	1.9	1.9	2.1	302	1302	94	306	94	138	45	45	50
Car	3172	12.7	54.8	4.0	12.9	3.9	5.8	1.9	1.9	2.1	403	1737	126	408	125	185	61	60	67
office	1212	12.5	68.0	5.3	8.7	1.3	1.8	0.6	0.9	0.8	152	825	64	105	16	22	7	11	10
office	1020	12.5	68.0	5.3	8.7	1.3	1.8	0.6	0.9	0.8	128	694	54	89	14	18	6	9	8
office	769	12.5	68.0	5.3	8.7	1.3	1.8	0.6	0.9	0.8	96	523	41	67	10	14	5	7	6
office	635	12.5	68.0	5.3	8.7	1.3	1.8	0.6	0.9	0.8	80	432	34	55	8	11	4	6	5

[(a)]Total BC was measured by using the AE-51 at 5-min intervals

Values agreed with previous reported sizes (Reddington et al., 2013, Cheng et al., 2014, Liu et al., 2014). However, differences were registered in absolute concentrations. For instance, during home activities higher concentrations were displayed in the kitchen, which has been reported to disclose high values on previous research (Figure XI-3) (Van Vliet et al., 2013, Buonanno et al., 2013b).

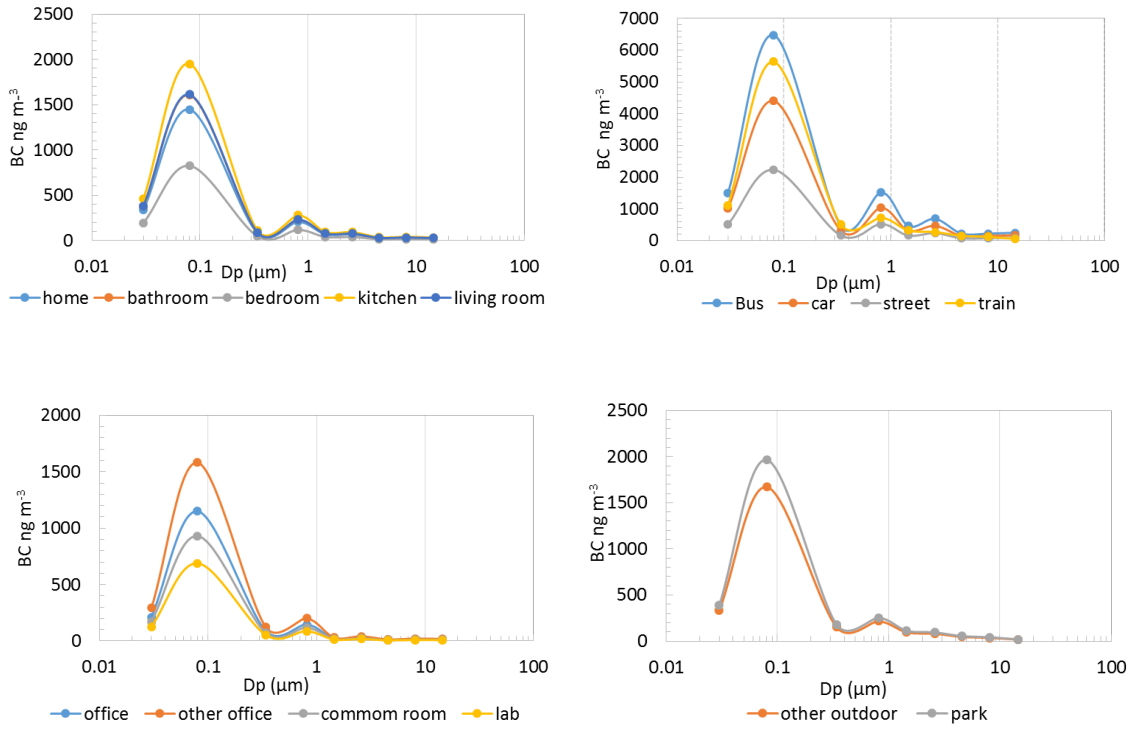


Figure XI-3 BC size fraction distribution obtained from the FIXAT BC concentrations.

Considering the commute mode, the highest concentrations were obtained for bus and train (Dons et al., 2012), while other office concentrations were higher than the volunteers' office and the outdoor levels. In general, the highest concentrations were obtained for transport mode (Dons et al., 2011, Delgado-Saborit, 2012, Buonanno et al., 2013b).

11.4.2 Lung intake – sensitive analysis (effect of the ventilation rate)

Lung intake (LI) was calculated using Eq. XI-2 and three different ventilation rates published. Figure XI-4 shows no statistical difference across the LI obtained for home, work or other indoors by using the three different VE (one-way ANOVA $p>0.05$). However, variations were registered in –transit, which can be because the VE used by the ICRP model and Loader for car, bus or train are the equivalent for sitting or rest, while (Int Panis et al., 2010) uses a specific VE for transport activities, with higher VE. Another factor that might influence the LI values is that walking, which is considered in the in-transit classification, reported VE of 49 L min^{-1} from (Allan and Richardson, 1998), which is higher than the used from ICRP model (25 L min^{-1}) and (Loader, 1999) (39 L min^{-1}). Based on the obtained results, the most specific ventilation rate, which includes most of the activities or level of exercise, were those reported by the ICRP model and these VE rates were used in the rest of the calculations.

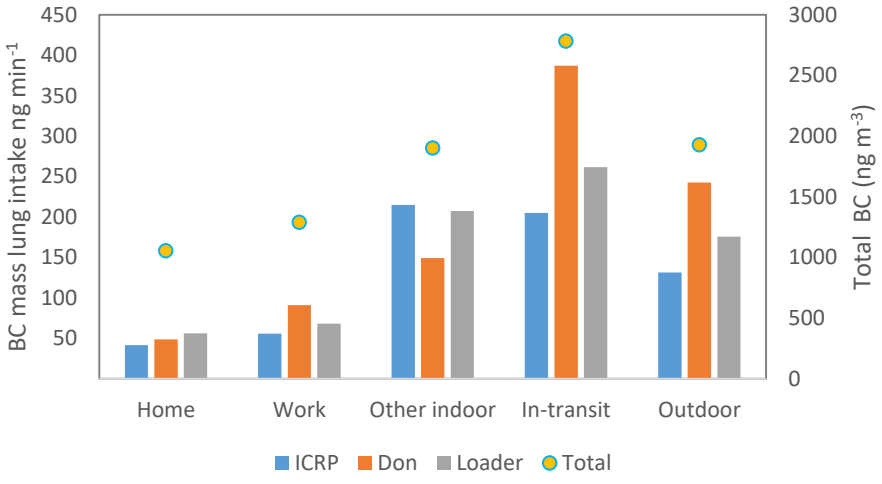


Figure XI-4 Comparison between the lung intakes calculated by using three different VE obtained from the literature and volunteers BC total average concentration per microenvironment (dots represent the total black carbon).

11.4.3 Lung intake (Gender-activity)

Lung intake (LI) mass was calculated using the ICRP VE. Higher LI was obtained for bathroom and kitchen locations, and this might be attributable to the high-observed concentrations BC in these microenvironments and the level of exercise. From the total BC at the bathroom location, it was observed that female LI was higher than male. Values will increase due to the high exercise by female subjects as normally they reported to be in the bathroom engaged in several activities like cleaning, having a shower, drying the hair, while male subjects reported only to shower. No significant differences were obtained between the LIs in the bedroom and living room as main activity was resting in both locations (independent t-test $p>0.05$) (Figure XI-5).

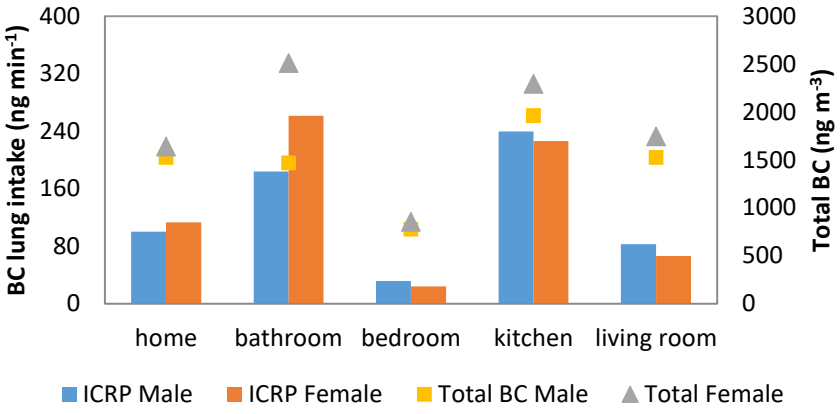


Figure XI-5 Home lung intake and total BC comparisons between male and female (dots represent the Total BC).

The difference in the level of exercise of the activities can be observed during time spent in the lab and common room, with higher LI for male than female (Figure XI-6). Although the lab BC concentrations were not as high compared with other office locations, the effect of the level of exercise can be observed in high LI at lab locations.

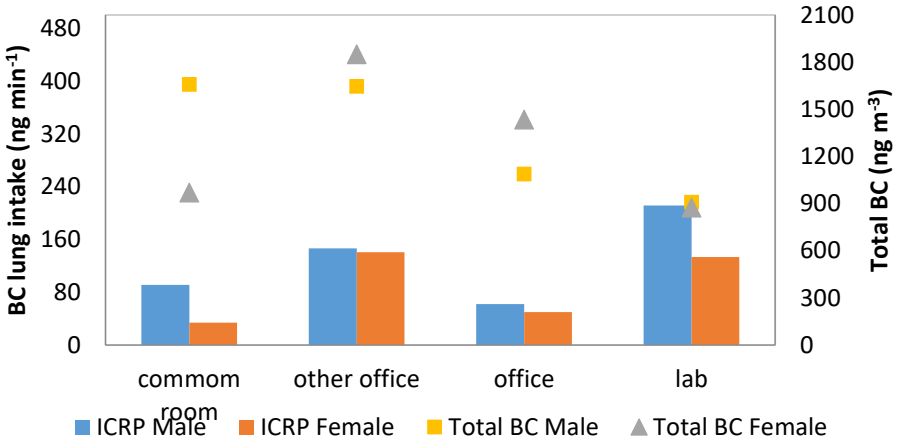


Figure XI-6 Workplace lung intake and Total BC comparisons between male and female (dots represent the Total BC).

The commute LI showed higher values during the use of bus for male subjects. The values most probably were influenced by the higher male VE and the high BC average concentration (Figure XI-7). Car LI was also higher for male subjects, while train LI was observed to be higher for female subjects. No statistical differences were observed in the LIs while subjects spent time in the street, although LI was higher than car and train.

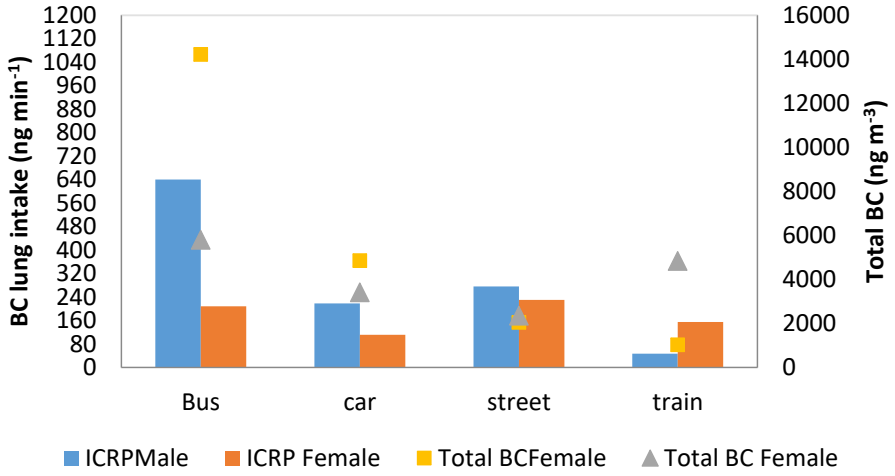


Figure XI-7 In-transit lung intake comparisons between male and female (dots represent the Total BC).

These locations were to be considered as not high air pollutants exposure locations, other indoor locations registered high LI values compared with office and home, reporting values close to 400 ng min^{-1}. In this case, females are more exposed as they spend more time in these microenvironments (Figure XI-8).

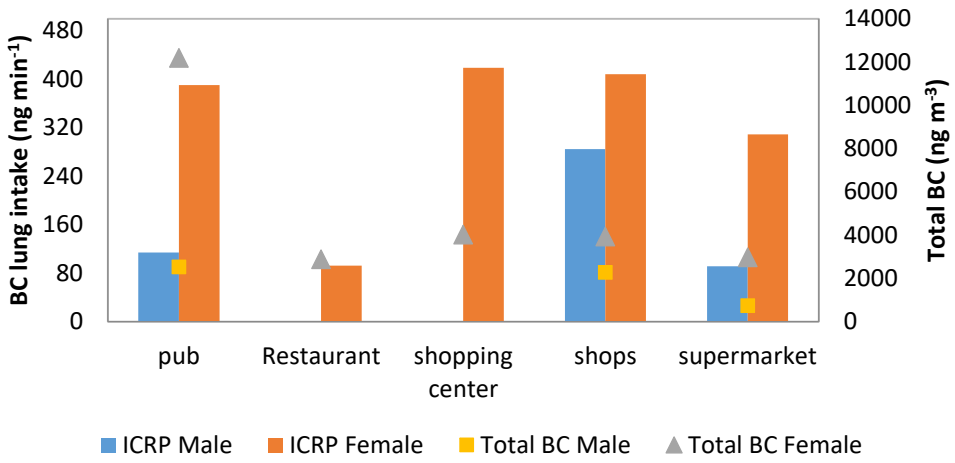


Figure XI-8 Other indoor lung intake and total BC comparisons between male and female (dots represent the Total BC).

11.4.4 Inhalation dose

The inhalation dose (ID) was calculated using the ICRP ventilation rates (Eq. XI-5). Despite higher levels of exercise and longer exposure time for women compared to men, there was no significant gender difference for home microenvironments in BC size fraction 0.08 μm (paired t-test $p>0.05$). For instance, females spent more time doing heavy exercises activities (12 %) while male level of exercise was distributed 37 % for light exercise and 63 % for resting. In addition, this was reflected in the obtained ID values for kitchen activities, which were 3.6 and 3.7 ng kg^{-1} day^{-1} for male and female respectively. Followed by bathroom, general home and living room (Figure XI-9).

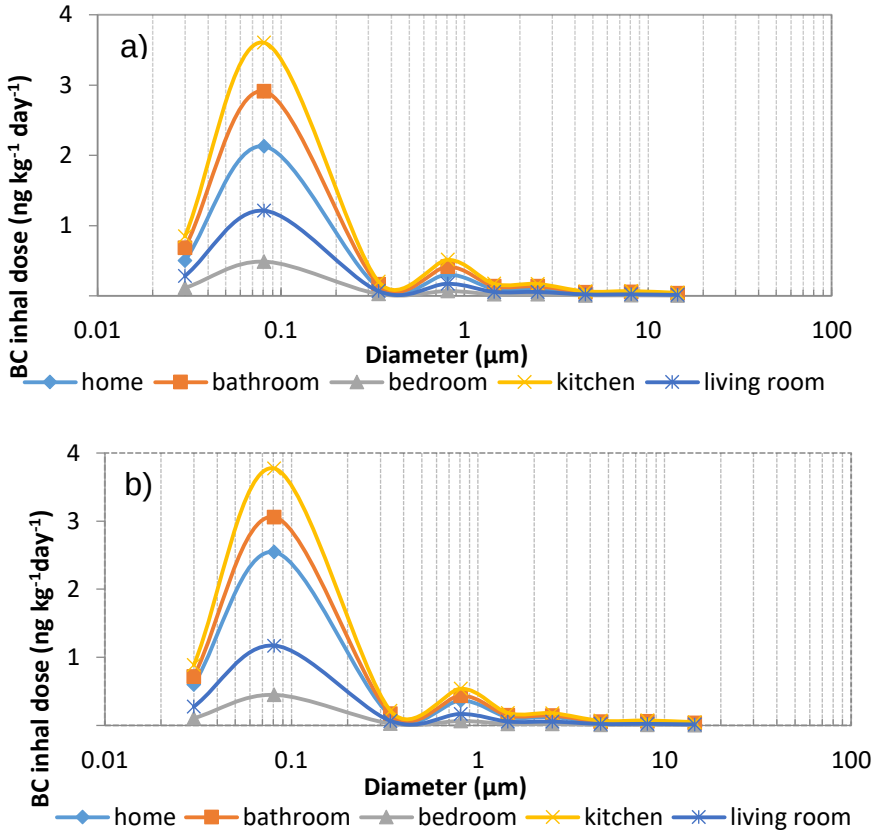


Figure XI-9 Gender comparison of the BC ID calculated by size fraction at home microenvironments a) male and b) female results.

The BC inhalation dose was also calculated for the office microenvironments (Figure XI-10). Primary peak was displayed at 0.08 µm showing a higher inhalation dose during lab activities with 2.6 ng kg^{-1} for males and 2.0 ng kg^{-1} for females. According to the data obtained from the questionnaires, on average, males spent less time at the lab (1.5 %) than the females (2.2 %). In this case, the effect of weight and ventilation rate over the lung inhalation results was noticeable.

Gender difference was observed in the common room with a higher inhaled dose for males (1.1 ng kg^{-1} day^{-1}) compared to females (0.49 ng kg^{-1} day^{-1}).

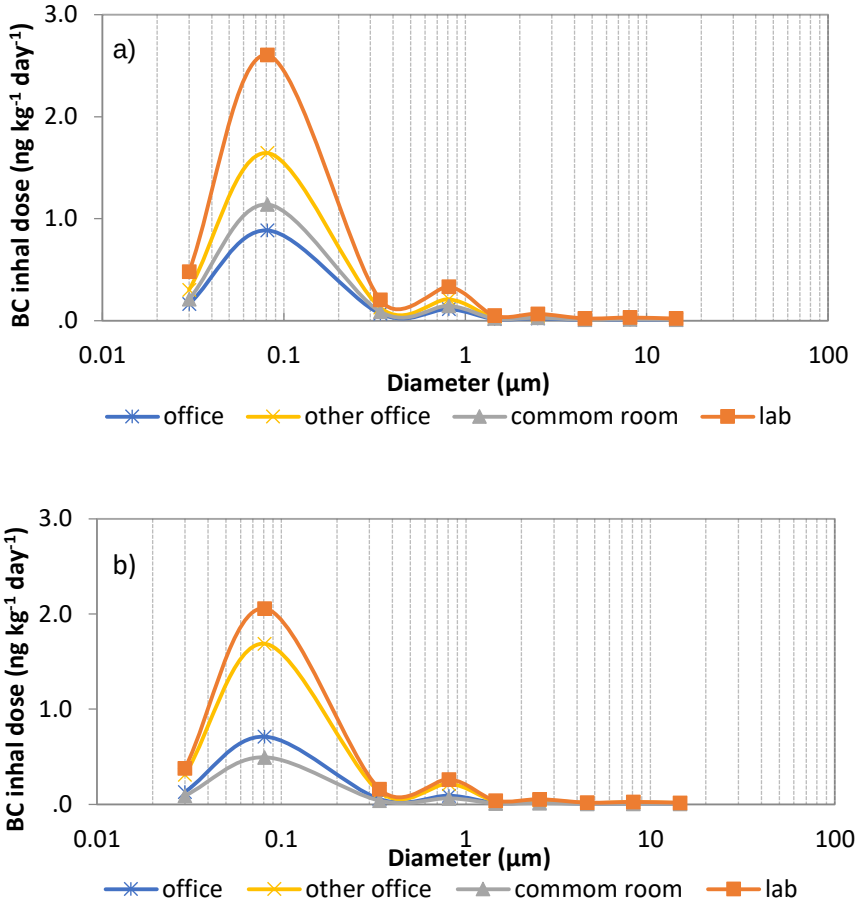


Figure XI-10 Gender comparison of the BC inhalation dose calculated by size fraction at office microenvironments a) male and b) female results.

Gender differences at in-transit microenvironments were found for the primary and second peak. Higher inhalation dose was obtained in car and bus for male with 7.9 and 3.1 ng kg^{-1} day^{-1} respectively (<0.1 µm), compared with female 2.3 and 2.0 ng kg^{-1} day^{-1}. However, for sizes greater than 0.1 µm (second peak), the bus inhalation dose was higher than the rest of the commute modes for males. Contrary to that for females higher inhalation rate was for train (4.17 ng kg^{-1} day^{-1}) at the primary peak (0.08 µm), while male registered only 0.92 ng kg^{-1} day^{-1} (Figure XI-11).

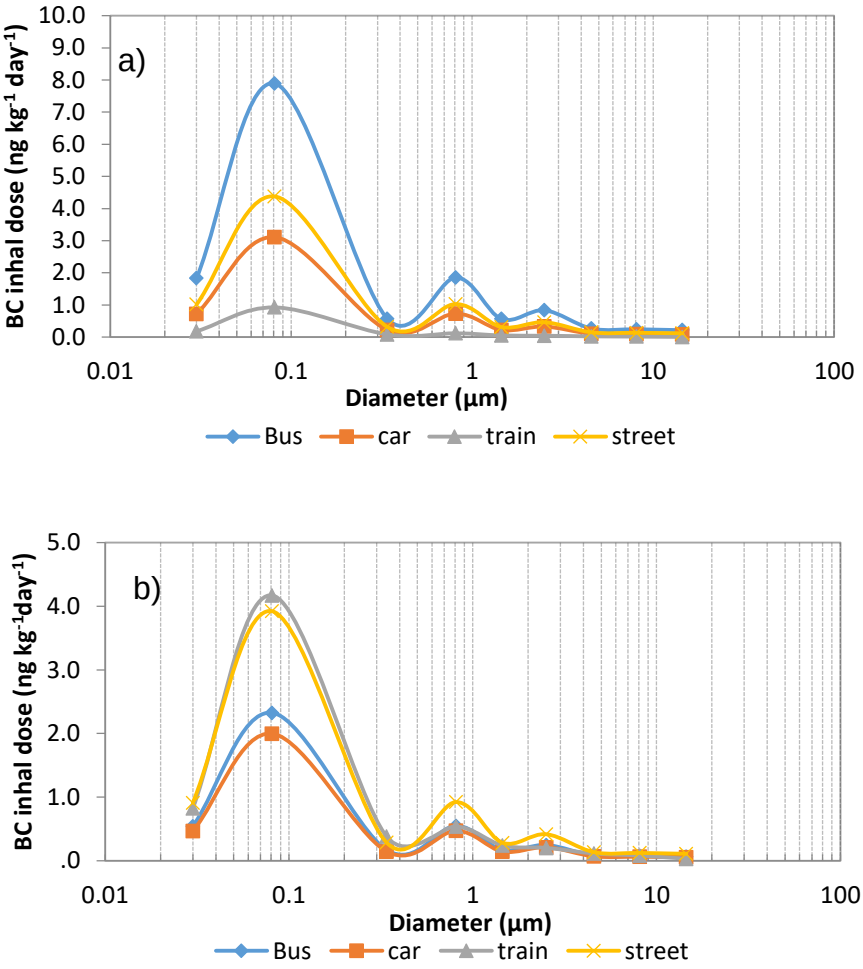


Figure XI-11 Gender comparison of the BC ID calculated by size fraction at in-transit microenvironments a) male and b) female results (GM).

11.4.5 Deposition efficiencies

The DE were calculated based on the equations obtained in section 11.3.6 and can be observed in Figure XI-12 to Figure XI-15 for light exercise, heavy exercise, sitting and sleeping respectively, which are specific for the MOUDI size stage.

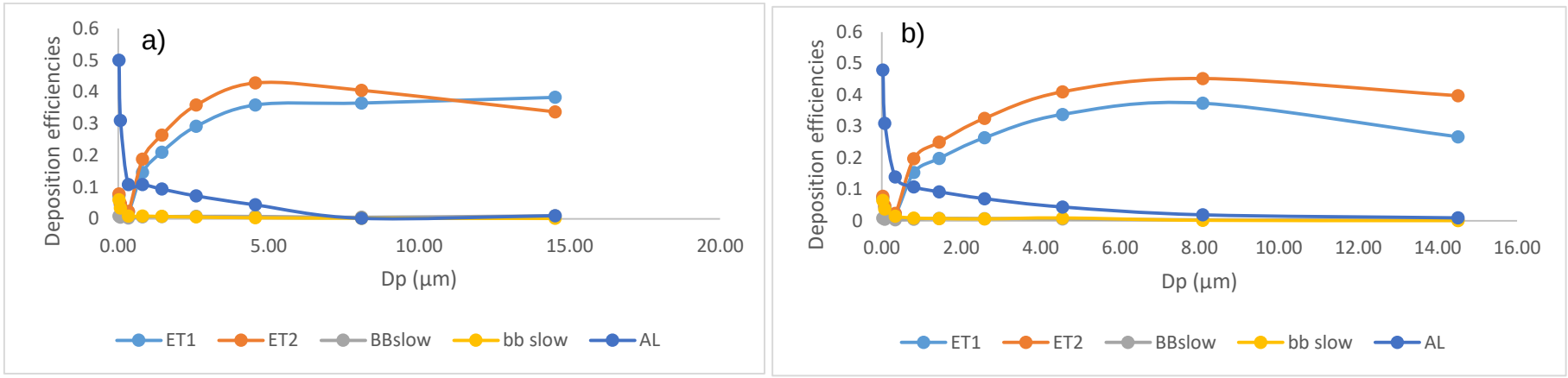


Figure XI-12 Particle size DE obtained from the MOUDI size and calculated using the equation obtained by plotting the DE of the ICRP model (light exercise), a) male, b) female.

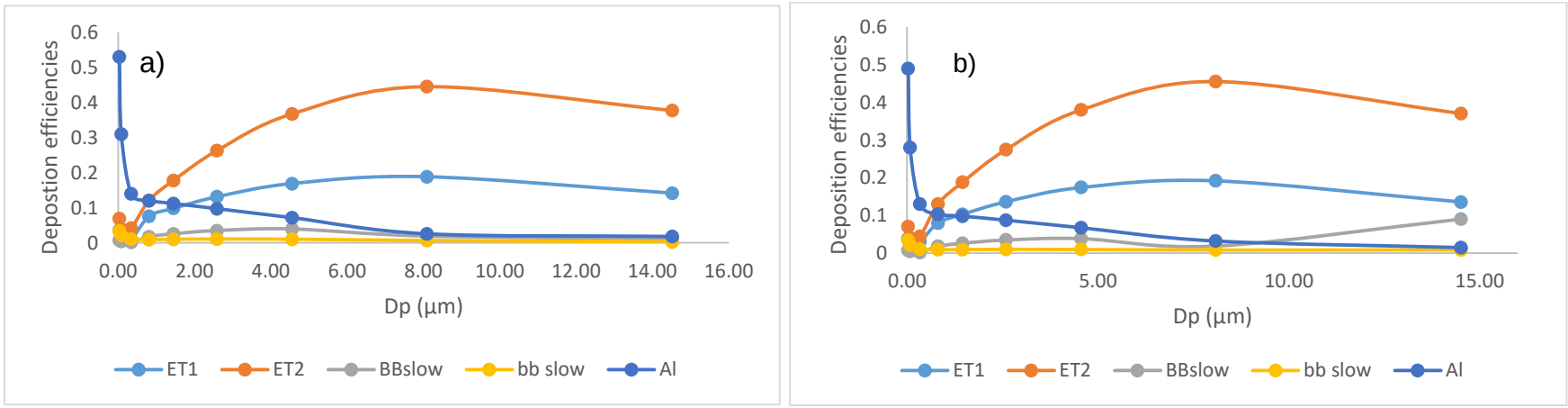


Figure XI-13 BC particle size Deposition efficiencies using the particle size obtained from the MOUDI samples and calculated using the equation obtained by plotting the DE of the ICRP model (heavy exercise), a) male, b) female.

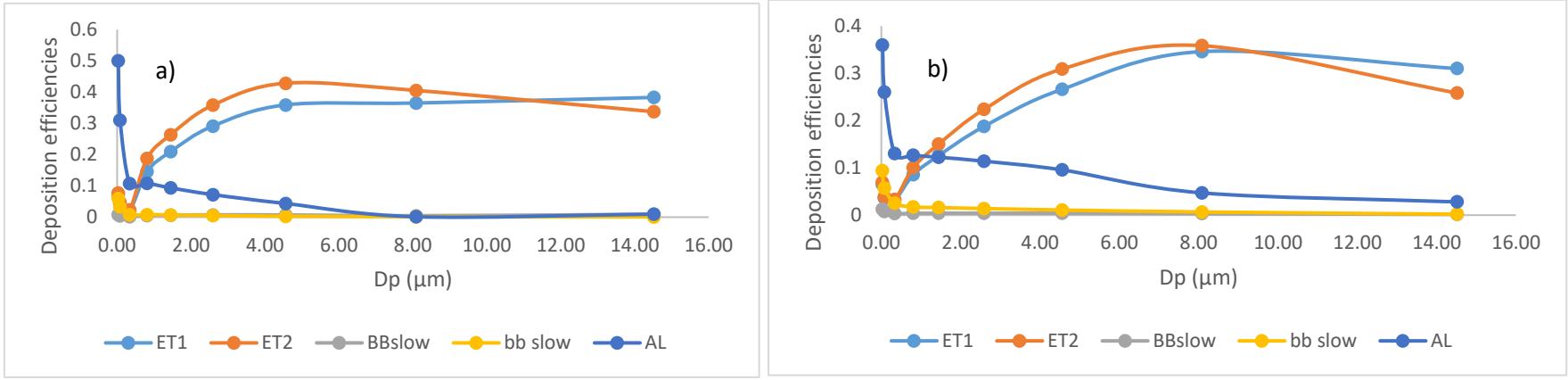


Figure XI-14 BC particle size Deposition efficiencies using the particle size obtained from the MOUDI samples and calculated using the equation obtained by plotting the DE of the ICRP model (sitting) a) male, b) female.

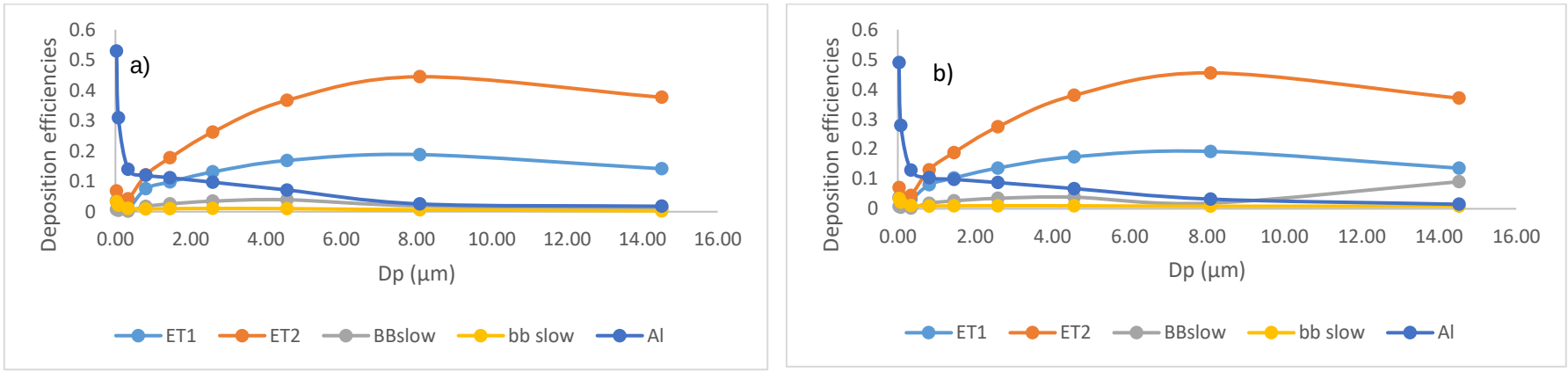


Figure XI-15 BC particle size Deposition efficiencies using the particle size obtained from the MOUDI samples and calculated using the equation obtained by plotting the DE of the ICRP model (sleeping), a) male, b) female.

11.4.6 Deposited dose

The deposited dose was calculated by gender because of the differences in the level of exercise developed by each and the resulting differences in ventilation rates and deposition efficiencies. Deposited dose obtained by using the ICRP ventilation rates and deposition efficiencies show multimodal BC size distribution in general. The primary peak was observed at 0.08 µm, followed by a peak at 0.8 µm and the third at 2.5 µm.

Higher deposited mass was observed for the alveolar region, and among commute methods, alveolar deposition for bus commuters was higher than car, walk and train transport modes. Male primary peak (0.08 µm) had a DD of 2.45 ng kg^{-1}, which was about four times higher than the female DD 0.62 ng kg^{-1} (Figure XI-16).

In general, BC concentration was higher for males (21667 ng m^{-3}) than for females (6671 ng m^{-3}) and this was also reflected in the DD (2.45 and 0.62 ng kg^{-1} for male and female). These differences can be attributable to the bus routes, since females mostly travelled on background roads. However, the level of exercise was the same for both genders. Diesel exhaust and wood burning are among the major BC sources (Rehman et al., 2011, Takahama et al., 2014). About the 70 % of the deposited particles emitted from diesel were under 0.1 µm and most of them reached the alveolar region. However, the concentration of carbon varies across the particle size fraction distribution (Oravisjärvi et al., 2014).

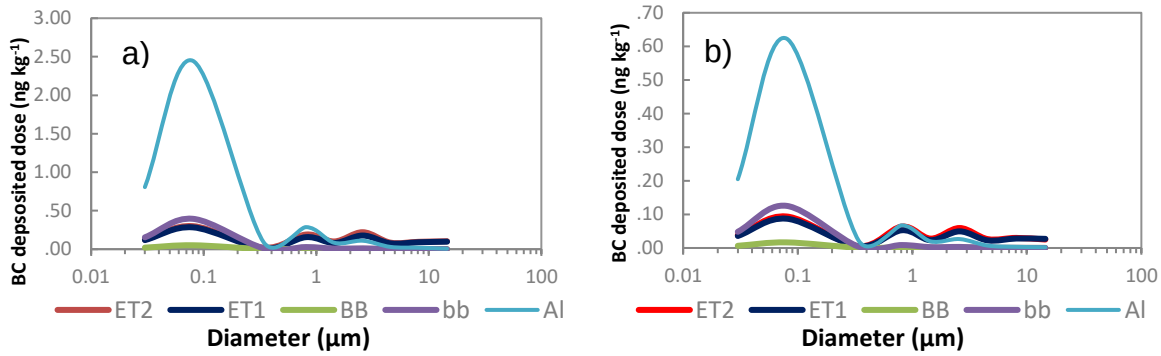


Figure XI-16 Bus deposited dose calculated in five regions of the respiratory track a) male and b) females results.

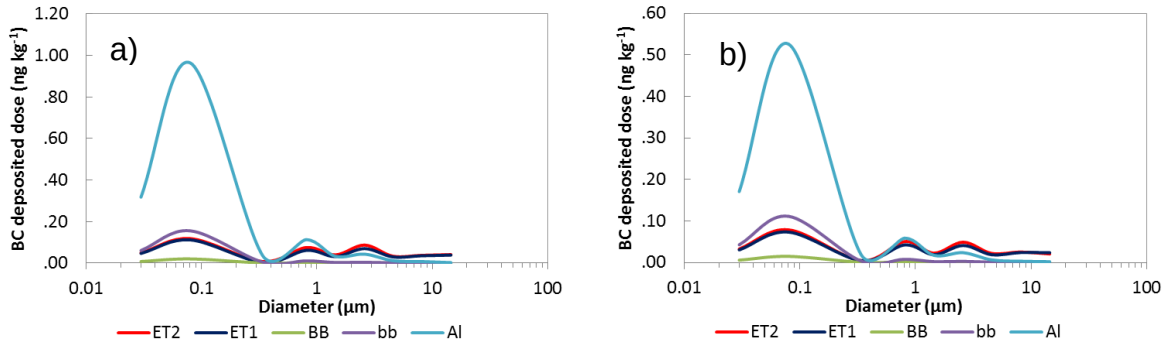


Figure XI-17 Car deposited dose calculated in five regions of the respiratory track a) male and b) females results.

Car BC DD was primarily in the alveolar region following almost the same trend as the bus. The primary peak was found at particles less than 0.08 µm for both (Figure XI-17).The effect of the corporal mass and therefore the VE was reflected in the male deposited mass (0.96 ng kg^{-1}), which was almost twice than female with (0.53 ng kg^{-1}). The number size distribution observed during traffic road emissions had a primary peak in the nucleation mode (0.017-0.018 µm), and a secondary peak was observed at 0.06-0.08 µm (Ruths et al., 2014). Nevertheless, the BC particle mass size for traffic

emissions has been reported mostly in the accumulation mode (0.1 to 0.5 µm) (Holder et al., 2014). Although no statistically significant difference was found between males and females, there was a difference in the total BC mass (8307 and 7664 ng m^{-3} for male and female respectively). Factors that might contribute to the total DD include: gender differences (body weight and VE), level of exercise (sitting or driving), road type (traffic and background) (Holder et al., 2014), temperature and air masses (Liu et al., 2014). BC concentrations have been related to traffic emissions and long term exposure is understood to decrease lung function (Suglia et al., 2008a).

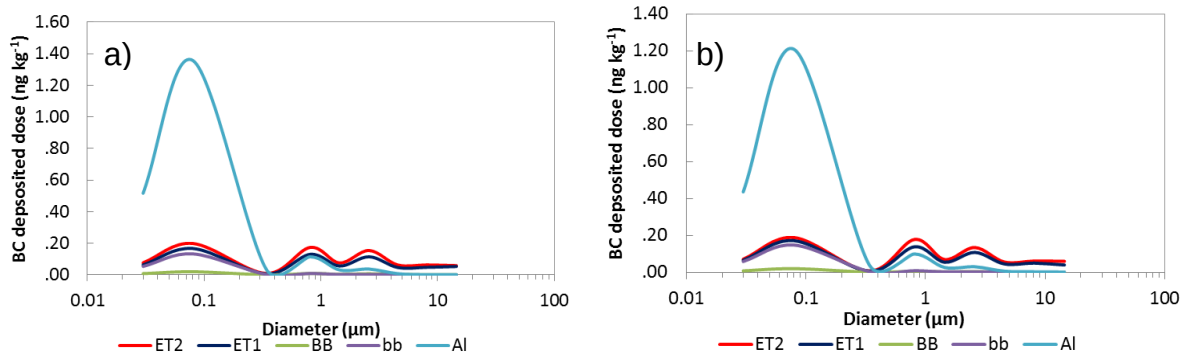


Figure XI-18 Walking deposited dose calculated in five regions of the respiratory track a) male and b) females results.

The BC mass in the street activities (Figure XI-18), which includes walking, cycling and waiting, was mainly deposited in the alveolar region for particles lower than 0.08 µm. It is known that exposure to BC might affect lung function during cycling more than other outdoor activities. Particle size fraction reported for cycling was 0.042 µm in Minneapolis, MN (Hankey and Marshall, 2015). The total BC concentration at 0.08 µm size fraction for female and male was observed to be 2314 and 2050 ng m^{-3} respectively.

The BC deposited dose in train does not show the same trend as other commute modes. Although alveolar regions had the highest deposited mass with a primary peak at 0.08 µm, the secondary and tertiary peaks were almost null (Figure XI-19). The gender alveolar deposition difference was observed to be caused probably by the total BC concentration obtained which was higher for female than male- 12309 ng m^{-3} and 2542 ng m^{-3} respectively. These concentrations sometimes includes the train station values as according to the TAD, female travels were from university to the city centre, while the male were reported to be out of the city centre.

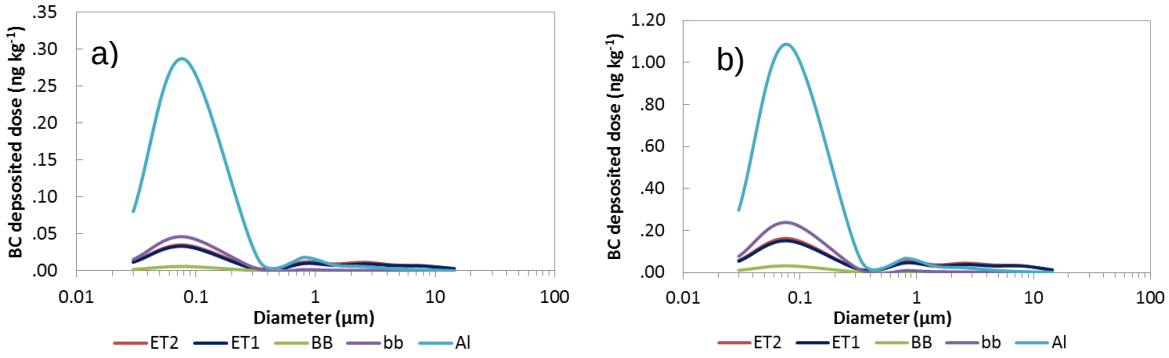


Figure XI-19 Train deposited dose calculated in five regions of the respiratory track a) male and b) females results.

In general, for home-based activities, deposited mass had the primary peak at 0.08 µm, followed by a secondary peak at 0.8 µm. However, the third peak in these home microenvironments was less visible compared with commute modes.

General home (Figure XI-20), includes activities done by the volunteers which were not in a specific place of the house, (frequent movement of place). Total deposited mass were for general home was around ± 0.06 ng kg^{-1} and for bathroom ± 0.08 ng

kg^{-1}. DD were in function of the concentration and level of exercise, which was reported as a low or just rest, displaying no gender difference (Figure XI-21).

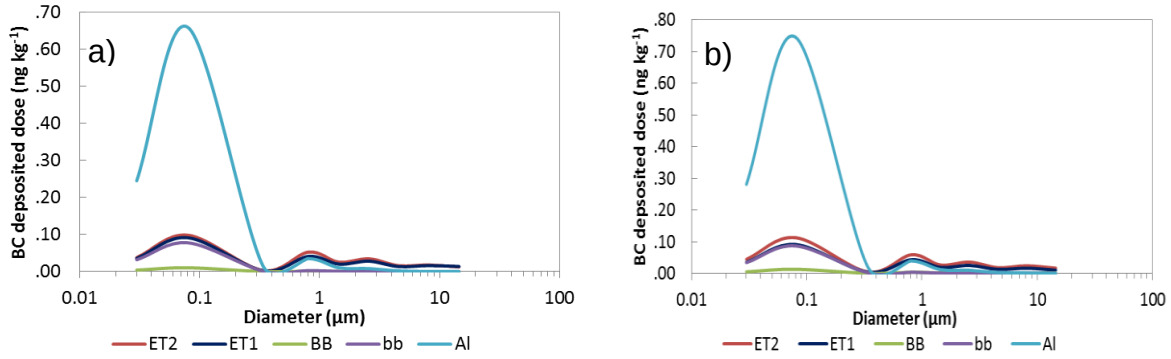


Figure XI-20 Home deposited dose calculated in five regions of the respiratory track a) male and b) females results.

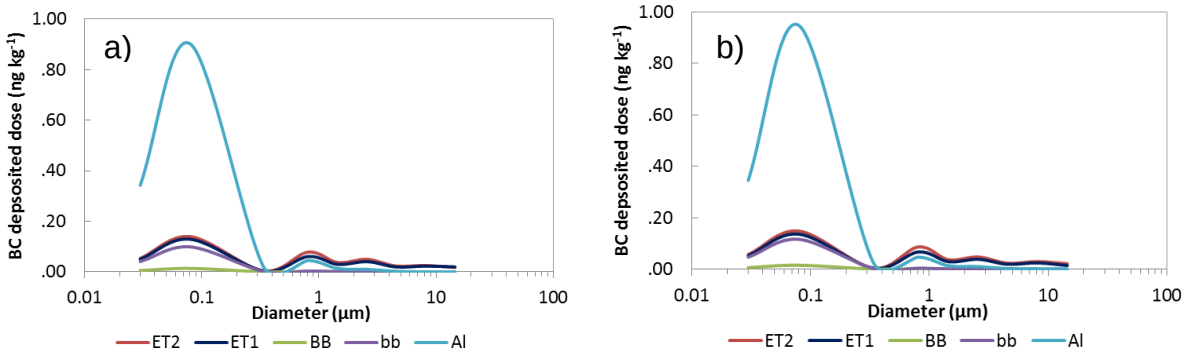


Figure XI-21 Bathroom deposited dose calculated in five regions of the respiratory track a) male and b) females results.

The lowest DD was observed while subjects sleep or rest (Figure XI-22). According to the TAD, even those microenvironments where the level of exercise was low (e.g. general home and bathroom), the VE was used for light exercise. On the other hand, there is a specific VE for sleep, coupled with it, BC concentration were much lower at the bedroom microenvironment (Figure XI-22).

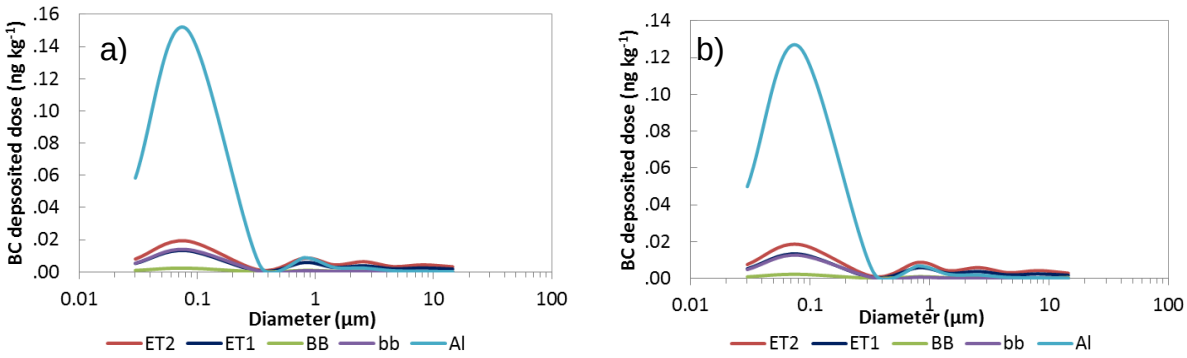


Figure XI-22 Bedroom deposited dose calculated in five regions of the respiratory track a) male and b) females results.

Kitchen (Figure XI-23), on the other hand, showed the highest values across the home microenvironments and no statistical gender difference was reported (independent t-test P>0.05). Main activities reported at this location were cooking; cleaning and dish washing which were reported as light and heavy exercise. BC total concentrations at this location were ~ 3000 ng m^{-3}. For PM, during a cooking period, subjects received 10 times more deposited particles into the lung compared to a subject in outdoor microenvironments, reporting higher DD from particles with Dp the same as those observed in our results (0.08 µm) (Mitsakou et al., 2007).

Although high BC concentrations were reported for living room, considering that the pollutants run from the kitchen to nearby room, less DD at the alveolar region for particles of 0.08 µm was obtained. (Figure XI-24) This might be mainly because living room activities were considered as a rest, for which VE values were between light exercise and sleep. Therefore, although the total BC concentrations were almost similar to those in general home and bathroom, the deposited mass was lower.

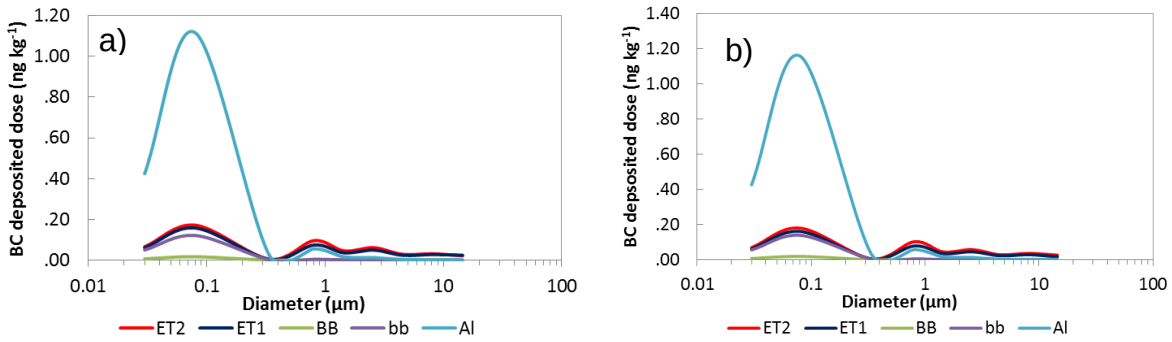


Figure XI-23 Kitchen deposited dose calculated in five regions of the respiratory track a) male and b) females results.

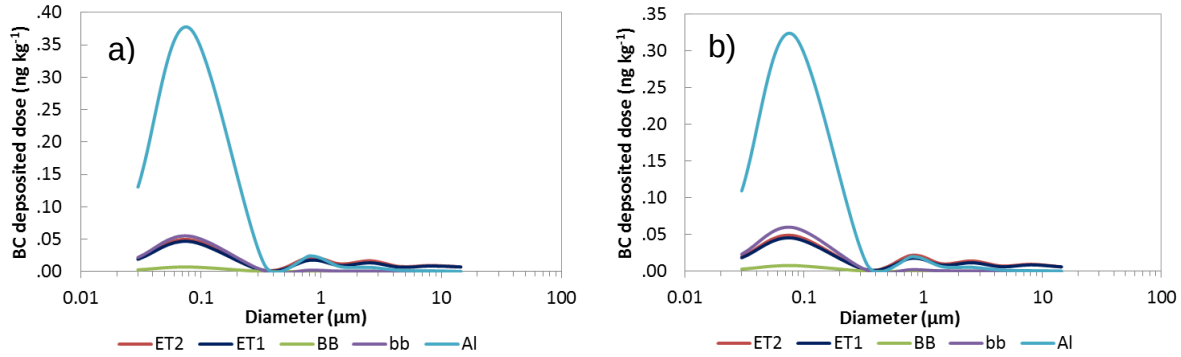


Figure XI-24 Living room deposited dose calculated in five regions of the respiratory track a) male and b) females results.

The primary peak for work place locations was also observed at 0.08 µm, with the highest deposited mass in the alveolar region. Similar values were obtained for PM size fraction on a working day, reporting higher mass at the alveolar region-1.0 µg, while for BB and ET, it was 0.3 µg and 0.2 µg respectively (Hussein et al., 2013). At these locations, the third peak was almost illegible. The differences were observed in the deposited mass; for instance, higher deposited mass (almost twice) was observed for other office (Figure XI-26) rather than their own office (Figure XI-25 y Figure XI-26). The level of exercise might influence the DD together with the total BC mass concentration. This is because while subjects for office locations indicated rest, for other visited offices, the movement between the places was considered as light

exercise. Together with it, the MicroAethalometer BC reading for the subjects transfer between places (although short, influenced the levels) was considered as other office. Therefore, the total BC mass was higher in other office than in their own office.

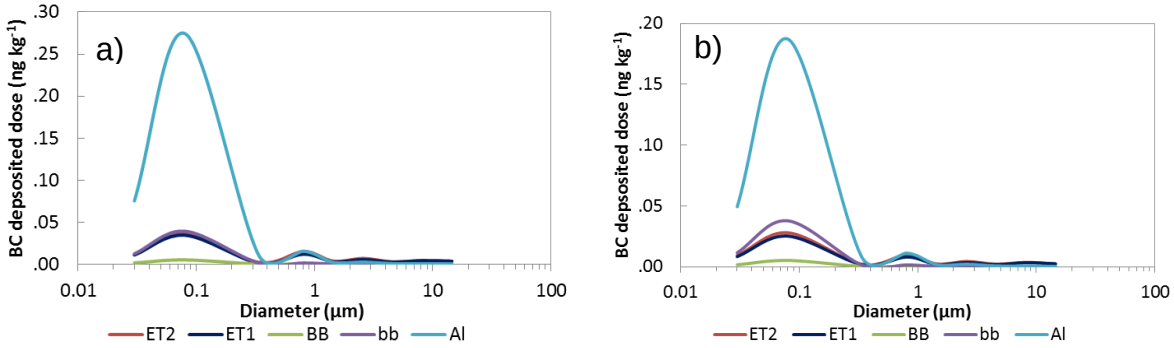


Figure XI-25 Office deposited dose calculated in five regions of the respiratory track a) male and b) female results

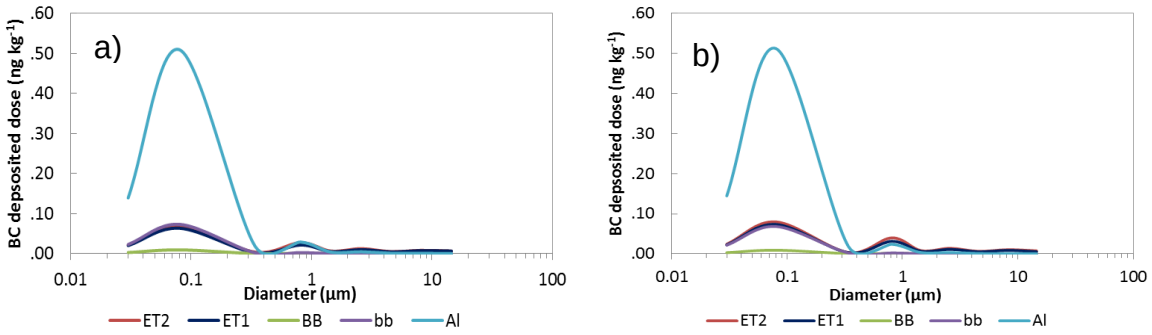


Figure XI-26 Other office deposited dose calculated in five regions of the respiratory track a) male and b) female results.

The effect of the level of exercise was also shown in the final DD at common room and lab microenvironments displaying a statistical DD gender difference. Most of the deposited mass was observed to be at particles with 0.08 µm in diameter at the alveolar region. Although, total BC concentration was almost similar, 1021 and 988 ng m^{-3} for female and male respectively, the DD for male (0.35 ng kg^{-1}) was higher than female (0.13 ng kg^{-1}) (Figure XI-27 y Figure XI-28). These differences were mainly because common room activities reported for female subjects were rest (having lunch, coffee

time or group discussions), while male subject reported light or heavy exercise activities. The same was also noticed for lab female (sitting) and male (light exercise). It is important to note that BC concentrations were close 1850 and 1143 ng m^{-3} (for both).

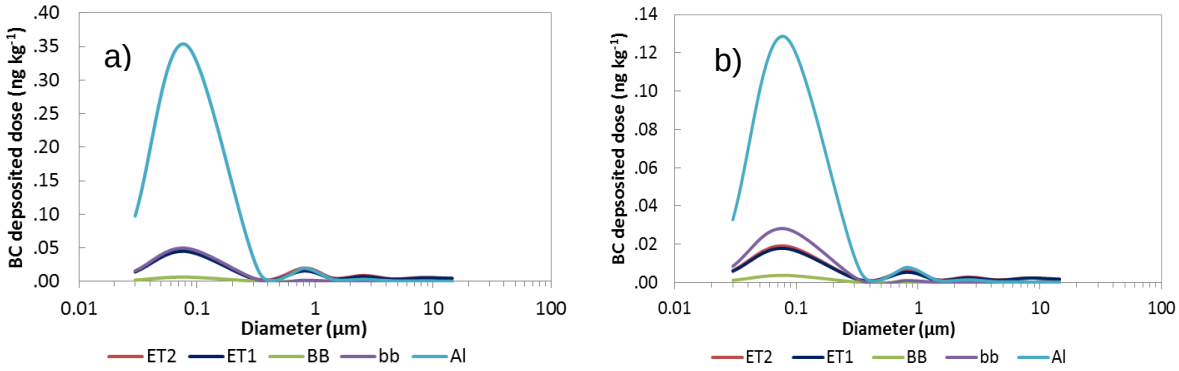


Figure XI-27 Office common rooms deposited dose calculated in five regions of the respiratory track a) male and b) female results.

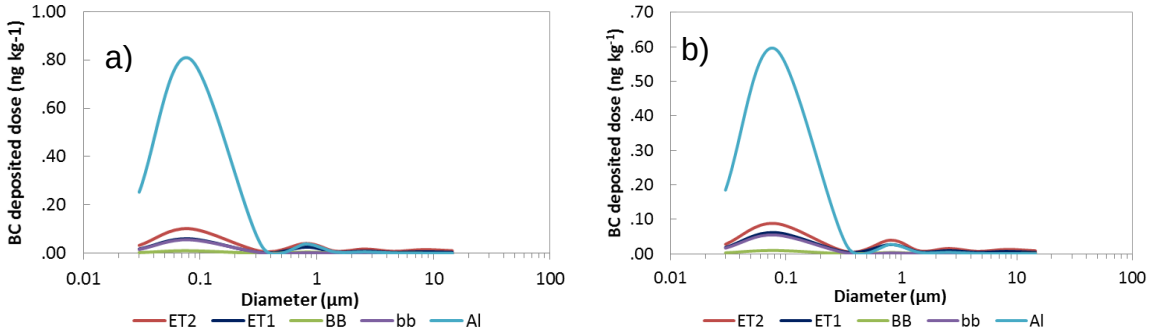


Figure XI-28 Lab deposited dose calculated in five regions of the respiratory track a) male and b) female results.

BC core diameter reported for London was observed to be ~0.1 µm from traffic emissions (Liu et al., 2014). It has been reported that the 0.2 µm submicron particle size is commonly found in smoking subjects, whereas in urban environments 5 µm can be observed (Balásházy et al., 2003). The reported BC size from traffic emissions ranged from 0.02 to 0.1 µm in Netherlands (Keuken et al., 2015). Previous studies

have reported the effect of the 2.5 μm particle size over the lung capacity, which was large when subject were exposed a sub chronic events (Chen et al., 2015, Gauderman et al., 2004, Knaapen et al., 2004). During personal exposure activities, subjects were mostly exposed to BC for longer periods. Moreover BC particles are known to be composed of other chemicals like PAHs which also contribute to the lung function decrement (Jedrychowski et al., 2015). In addition, PM can contribute to the deposition of mutagens, reporting that about 95 % of the mutagens deposition is produced by the ultrafine and fine particles emitted by road the side, urban and suburban environments into the alveolar region (Kawanaka et al., 2011). Because, the influence of the PM composition and source, it is not clear which factor is responsible of respiratory health effects or even of lung cancer (Knaapen et al., 2004). BC particles as can be observed in this study had the higher mass deposited in the alveolar (Al) region, and this is in accordance to what has been reported for PM showing higher for Al than for the TB region (Majid et al., 2011, Oravisjärvi et al., 2014). Therefore, it's important to consider BC particle size distribution.

11.5 Summary of main findings

Measurements from the microAethalometer (AE51) were used to obtain the deposited dose from the BC concentrations. Total BC from FIXAT subjects was split into various categories using the percentage obtained in BC deposition size fraction distribution (CHAPTER X) and the ventilation rates and DD formula were taken from the ICRP model (ICRP, 1994). VE was selected based on the comparison study (section 11.3.3 of this chapter) since the ICRP VE covers more of the volunteer's activities.

Inhalation and deposited dose were dependent on the BC concentration, level of exercise, particle size and exposure time, gender and body weight. However, these factors were associated with the visited locations and activities performed by subjects.

A bimodal BC fraction distribution was observed showing a primary peak at 0.08 µm followed by a secondary peak at 0.8 µm for all the tested environments. In general, the highest deposited mass was in the alveolar region showing higher DD for bus commutes and kitchen activities. Previous studies have found that in extreme events (e.g. short term traffic peak and cooking exposure), PM concentrations speedily increase in seconds, while the decrease is more gradual (Manigrasso and Avino, 2012). Consequently, the PM deposited dose behaviour in the extreme events seems to be similar to the BC deposited dose obtained in this study. The particles size ranges (fine mode) are between the BC size fractions and therefore the most abundant mass is deposited at the alveolar region.

The DD was primarily influenced by the subjects' transit locations. It is known that traffic emissions are the major source of BC (Apte et al., 2011, Dons et al., 2011, Cheng et al., 2014). The difference between genders can be attributed to the bus route type since higher DD was observed for male subjects, for whom primarily routes were traffic

roads (2.5 ng kg^{-1}) compared with females for whom routes were background roads (0.60 ng kg^{-1}). Train travel characteristic registered in the TAD showed the opposite trend- females had a higher DD (1.0 ng kg^{-1}) going from university to city centre while males had a lower DD (0.30 ng kg^{-1}) travelling from university to the sub urban areas.

Gender differences were observed by considering the level of exercise as a factor, as the VE is a function of male/ female VE. Females obtained higher DD at home as a higher level of exercise was reported compared with males. On the other hand, lab activities registered higher DD for males as a higher level of exercise was registered.

The source of exposure has a significant effect on the level of DD over the subject even without considering the gender. This can be observed in the higher DD obtained for kitchen and the lower DD for bedroom. Lower concentrations at bedroom had also been reported by (Dons et al., 2011).

The PM particle size distribution determined for traffic road samples showed that a primary peak between 0.1 and 1 μm, and this observation is similar to the results obtained for BC particle size distribution. The higher mass deposited was reported to be in the ET region for PM for ambient samples (Harrison et al., 2010, Taiwo et al., 2014). However, BC registered the highest deposition in the alveolar region, similar to our results, the authors had reported PM values that were taken from traffic peak hours showing that the mass was mostly deposited at the alveolar region and less DD was observed for the BB region (Manigrasso and Avino, 2012).

Based on the results reported for PM and carbonaceous material size distribution, fine particles dominated the Al region while coarse particles dominated the ET region (Aleksandropoulou et al., 2008, Aleksandropoulou and Lazaridis, 2013). During a

cooking event, the indoor size distribution showed the primary peak at 0.1 μm and was more abundant in the alveolar region (Mitsakou et al., 2007). Higher concentrations of BC are expected during traffic peak hour and cooking exposure. Consequently, the PM deposited dose behaviour in the extreme events seems to be similar to the BC deposited dose.

PM behaviour on human health has not been completely clarified as a wide range of factors will contribute to the effects, and considering that BC concentration in the air have been investigated to have more adverse health effects on the population. The importance of investigating the BC size fraction distributions and therefore the deposited dose, will contribute to understand the nature of the pollutant as its characterization will depend on the local activities, culture, climate, source, socioeconomic factors etc. These factors will help to reflect the real effect BC has on human health. Although these results are specific to population types with similar characteristics, the results can be used to contribute to epidemiological analyses to determine the influence of the pollutants on human health. Moreover, the obtained results can be used to development and/or refinement of models to predict the exposure not only in outdoor environments but also in indoor microenvironments and personal exposure.

GENERAL CONCLUSIONS

Epidemiological studies based on ambient or indoor monitoring data might under or overestimate the risk of exposure. Alternatively, using personal exposure measurements can help to improve estimates of risk for a group of people who share similar characteristics such as; demographic, socio-economic, cultural, geographic and climatic. (Bekö et al., 2015, Buonanno et al., 2014, Gens et al., 2014, Li et al., 2015a, Su et al., 2015). These characteristics will influence the type of activities conducted by the subjects, as well as the indoor and outdoor sources of pollution, atmospheric processing of primary pollutants, atmospheric transport of pollutants within the local and regional scale, as well as the indoor/outdoor infiltration and penetration of pollutants, which ultimately would influence the concentrations measured at the personal exposure level. Therefore, it is important to define such characteristics in the study group in order to assess the transferability of the results obtained in personal exposure studies, such as the one presented here, to other population demographics.

Although, it has been well studied that people on average spend more than 90-70% indoors (Harrison et al., 2009, Borgini et al., 2011, Dons et al., 2011) and that the most polluted microenvironments are kitchen, living room, and restaurants; the concentration on those microenvironments can change among sampling population groups (Lim et al., 2012, Steinle et al., 2013, Wang et al., 2009) and hence it needs to be characterised for the population considered in this study .

The results presented in this study refer to exposures measured in a group of healthy, non-smoking adult volunteer subjects, whose occupation is mainly office workers and students, living in urban and suburban areas within Birmingham, a large city in a developed country with temperate maritime climate. These characteristics should be

considered when assessing the results of the study, since similar population in countries with a different degree of economic development; or countries with hotter or colder climates will have different sources of pollution (Guo et al., 2015, Diapouli et al., 2010, Li et al., 2015a, Garrido et al., 2014), different exposure patterns in the population (Jedynska et al., 2014, Li et al., 2015b, Souza et al., 2014), and different outdoor/indoor exchange ratios for pollution (Balmes et al., 2014, Bekö et al., 2015). In addition, different groups of population (e.g. children, infirm) would have different exposure patterns, and hence different exposure concentrations, than those identified in the present study (Byun et al., 2010, Delgado-Saborit et al., 2011). Despite it would have been ideal to include other groups of population within the study, or population with other characteristics (e.g living in rural areas), the scope of work that can be conducted within the framework of a doctoral thesis is limited. Nonetheless, the results presented in this work, including various sensor validation experiments; characterisation of personal exposures in a panel study and several experiments aimed at characterising VOC decay rates and BC lung deposition are appropriate for the scope of a doctoral study.

In general, personal exposure studies reported in the literature had been carried out considering a small sampling population (Bekö et al., 2015, Chen et al., 2012, Demirel et al., 2014), and avoiding having many confounding factors that can bias epidemiologic interpretation. Those studies can help to estimate the potential health risk of subjects following almost similar activities patterns (Ashok et al., 2014, Choi and Spengler, 2014). This is because personal exposure concentrations reflect the role of various variables that can influence total concentrations such as ventilation, temperature, time of the day and year (Stocco et al., 2008). Therefore, it is important

to quantify personal exposure under different scenarios. Comparing the results of the current study with results reported in a number of personal studies reported in the literature conducted in several countries, the current concentrations are in agreement with similar conclusions on the personal exposure range, and the risk of specific microenvironments visited by subjects. This is true, even after considering the specific characteristic of the population in this study, which might vary from the population characteristics specific to other reported studies.

Overall, this study found the most polluted microenvironments evaluated during the personal exposure studies were the kitchen, living room and garage; despite ambient concentrations or reported subject activities being different. This finding is broadly in accordance with existing literature on the topic (Buonanno et al., 2014, Van Vliet et al., 2013). On the other hand, caution should be exercised, since there are many characteristic specific to a location and group of subjects, as listed above that can influence exposure. Hence, in similar countries or even other locations within Birmingham with subjects having similar time activities patterns, it cannot be generalized that the highest concentrations would occur in those microenvironments if the outdoor or indoor sources are different.

Even this type of panel studies cannot be easily applicable to sample large populations due to economical and logistical reasons, and although several limitations exist in the current design which can add a certain degree of uncertainty (e.g. low confidence in the oxy-PAH results), and also considering the specificity of the results to the demographic group of study, which makes the scope of this study restrictive, the results presented in this work will still contribute to fill the gap of the importance of the personal exposure.

Novel sampling technology has been developed to meet different sampling criteria (Chen et al., 2012, Delgado-Saborit, 2012, Tsow et al., 2009, John et al., 2013), such as: type of pollutant, compact instruments, longer battery life, low weight, GPS incorporated etc. (Su et al., 2015). Considering the benefits in characterising personal exposures, the necessity of having more portable instruments has increased in recent years. Although some studies have concluded that measuring exposures of subjects at the individual level is impractical, personal exposure measurements are still the best measurement to characterise subject's true exposures to air pollution (Du et al., 2010, Steinle et al., 2015).

Therefore, more studies are needed to test the accuracy and precision of novel sensors as they emerge. In this study two sensors were tested for two types of pollutant types: the TVOC online sensor for VOCs (recently released by the University of Arizona, ASU) and the MicroPEM for measurement of $PM_{2.5}$ developed by scientists from RTI International. Based on the results from the inter comparison exercise, the $PM_{2.5}$ concentrations measured by the sensor and the gravimetric filter were higher than concentrations measured at the central site (CS). However, good correlation was observed between the sensor and the CS, while the gravimetric concentrations reported lower correlation with the CS.

On the other hand, for VOCs, the correlation between the TVOC sensor (ASU) and the integrated samples (sorbent tubes) showed a correlation coefficient of 0.83 using the cumulative concentrations of the tube samples. However, in this particular case, the sensor concentrations were observed to be higher than the integrated samples and the differences can be due to the sensor sensitivity to any VOC present in the atmosphere, whilst integrated sample will account only for specific VOC analysed in

the CG-MS. Other factor that might influence the concentrations is the difference in limits of detection, having lower limits when the integrated sample is used. Thus, it can be concluded that although real-time sensors are a good tool for personal exposure, further investigation needs to be conducted to properly use such instruments as an alternative method to test pollutants. In this respect, the already established laboratory method can be the best option to characterise VOC, especially when individual VOC are required to be characterised. However this is achieved at the expense of losing time resolution, and entails a sophisticated and expensive analytical protocol. On the other hand VOC concentrations depend on the activities, sources, and locations just to mention a few (Evtyugina et al., 2014, Rackes and Waring, 2015, Su et al., 2013, Civan et al., 2015). Hence, the TVOC sensor will offer the possibility of high time resolution concentrations, which would be useful to characterise which activities emit the highest VOC concentrations.

In this study, two hypotheses were tested: the influence of construction products on the VOC concentrations and the differences in VOC exposure based on locations and activities. For the former, higher concentrations were observed for new or recently redecorated houses. However, higher differences were observed when samples were taken during the first days of redecoration, as observed in a study of recently remodelled offices where compounds decay with time (10 days). However in the FIXAT study, where samples were taken from 3 different groups, and considering different level of exposure, a difference was observed between new and old houses, but it was not statistically significant. This might be attributable to the fact that the sampling criteria considered a “new house” those where sampling was conducted within a period corresponding to less than 3 months since the house had been constructed or

remodelled. In general, office concentrations showed higher values than personal exposures and home (McCreddin et al., 2013, Rackes and Waring, 2015), and this is mainly because the number of sources found in the workplace area, such printers, cleaning products, carpeting, number of occupants and furniture needed for each occupant, poor ventilation, which might be higher in offices than in houses; coupled with this, the infiltration of outdoor pollutants is considered a high contributor of personal exposure pollutant levels (Demirel et al., 2014, Jo and Kim, 2010, Terry et al., 2014) measured in the offices.

Based on the results, further studies need to be developed on new or recently redecorated microenvironments indoors, considering factors such as temperature, activities, ventilation, outdoor sources, since those might be a factor that might increase or decrease the decay rate. The aim of such studies would be to find the combination of parameters that favour a large decay rate to ensure the rapid decrease of VOC concentrations to reach levels that might not cause negative health effects on building occupants.

Likewise it has been reported that homes are the microenvironments that highly contribute to the PAHs exposure (Gariazzo et al., 2015). FIXAT results concentrations were observed to be higher at work microenvironments for some of the compounds, suggesting the influence of outdoor sources (such as construction and traffic emissions) more than indoor activities (Kliucininkas et al., 2011, Wei et al., 2010, Yan et al., 2015, Wu et al., 2014). However, this cannot be generalized. In this particular case most of the sample subjects worked on the University Birmingham campus and other subject's offices were localized near to traffic roads. It is well known that combustions processes will highly contribute to personal exposure together with the

intensive use of cleaning and aromatizing products used during the cleaning activities at the offices. Even more, during the sampling period there were several construction activities in development in the main campus of the university. Based on the sampling questionnaires, most of the offices faced the internal road and the construction increased the exposure. All the above factors were highly reflected in the office results and contributed to the personal exposure concentrations. It can be observed that the importance of personal exposure measurements as subject's exposure will vary depending on the time of exposure at work and frequency of contact with different pollution sources. Epidemiology studies based on indoor activities such offices (in this case) will overestimate the exposure.

Concentrations of oxy-PAHs measured indoors were higher than previous measurements at outdoor locations in Birmingham UK (Alam et al., 2013b, Alam et al., 2013a, Saborit et al., 2009). However, whilst VOC and PAH concentrations reported in this study are characterised with a high degree of confidence, quality assurance and quality control protocols suggest that oxy-PAHs measured in this study were less accurate and precise. Hence the results and interpretation from the oxy-PAH samples should be considered with caution.

Further research is suggested to characterise indoor and personal exposure to oxy-PAH concentrations using an improved sampling and analytical methodology that would result in higher accuracy and precision of oxy-PAH concentrations. In addition, further research needs to be conducted to determine if concentrations were generated at the indoors or at the outdoors. This can be achieved using source apportionment analysis. Also further studies need to be developed to understand the indoor sources and behaviour of oxy-PAHs indoors as most studies have mainly focused on outdoor

characterisation. However, the current results suggest that subjects might be highly exposed to oxy-PAHs in indoor environments, especially during day time. Nonetheless, this finding would need to be corroborated with an analytical protocol that ensures higher degree of confidence in the oxy-PAH results.

The highest BC personal exposures measured with the microAethalometer were observed while subjects commute and cook. Nonetheless, higher concentrations were also observed when subjects visited petrol stations. It has been well studied the contribution of combustion processes to the exposure to BC, however it is necessary to identify how other factors such as outdoor ambient concentrations, ambient temperature, and indoor/outdoor ventilation will affect personal exposures.

In this thesis, a novel methodology to measure BC size fraction was proposed by using the MOUDI and smoke stain reflectometer, considering the relationship between the BC, BS and EC. However, although the MOUDI instrument was placed outdoors at the houses, the heavy weight, large size of the instrument, and generation of noise from the pumps of the MOUDI makes it difficult to collect samples in indoor environments. However, the proposed methodology can be used outdoors or even further consideration might be given to using small sampling instruments (Guo et al., 2015). The inter-comparison results showed a good correlation between the reflectance and absorbance using Teflon and filter paper. Therefore, equations suggested to estimate BC using filter papers can be used to estimate BC when a Teflon filter was used, applying the correction factor obtained between Teflon and paper filter readings. Once the methodological approaches have been defined, the main aim was to calculate the BC size distribution in order to determine BC lung deposition.

In general, BC particles were largely distributed between the Aitken and the accumulation mode, affecting primarily the alveolar region. In addition to well-known parameters such as environmental concentrations and level of exercise, this study has found that locations visited and behaviours, such as commuting and cooking, increases the amount of deposited dose. Results from this study showed that the amount of deposited dose will depend on the type of transport used and the routes taken. Cooking will affect the deposited dose depending on the cooking style, kitchen design, and subject behaviour (e.g. turn on the fan or opening a window to increase ventilation). Whereas BC personal exposure concentrations was the lowest for walking among all the traffic modes, the inhalation dose associated to walking was the highest (Li et al., 2015a).

Based on the above results, further investigation needs to be conducted to understand the behaviour of the studied pollutants and to consider different characteristics such as socio-economic, ambient conditions (e.g. local wind speed, temperature, and humidity), individual characteristics (e.g. age, gender, health, genetic background) and personal time-activity patterns. More portable instruments are needed to collect samples without causing concerns or obstruction to the sampling populations.

Little research had been conducted considering personal exposure and in most of the cases some of the studied characteristics are different to this study, such as temperature, season, time scale, subject's behaviours, cooking style, traffic dynamics etc. making it difficult to properly compare personal exposure concentrations of air pollutants with other studies as the sampling environments are highly variable. It is advisable to highlight the importance of considering personal exposure and lung uptake concentrations to inform epidemiological studies as the basis to estimate the

human and ambient risk produced by the acute or chronic exposure to air pollutants. Personal exposure studies like the current study, even considering the limitations to extrapolate the conclusion to the general population, provide relevant information and evidence to help characterise human exposures to such pollutants.

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